

CRYOGENICS

An International Journal of Low Temperature Engineering and Research

VOL. 1 NO. 2

DECEMBER 1960

Recent Developments in Gas Cryogenics

H. O. McMahon *Arthur D. Little, Inc., Cambridge, Mass.*

Received 2 September 1960

TEMPERATURES below approximately 10°K can be obtained only through the use of helium gas as a refrigerant. Moreover, in order to liquefy helium it is necessary to compress the gas to approximately $200\text{--}300\text{ lb/in}^2$, cool it to approximately 15°K or colder, and expand it through a Joule-Thomson cycle to 1 atm or less. All liquefiers or refrigerators must necessarily have this feature in common. Refrigerators differ from each other according to the way in which the initial cooling from 300°K to 15°K is accomplished.

The classical method, and the one first used to liquefy helium over fifty years ago,¹ utilized the boiling of liquefied nitrogen and liquefied hydrogen under reduced pressure as the method of precooling. For liquefying batches of helium this method is still used in some laboratories which have an adequate supply of liquid hydrogen. However, it is not an attractive method for producing refrigeration continuously in a closed cycle.

A considerably improved method of providing precooling without using any refrigerants other than helium was developed by Collins,² and has led to the widely accepted ADL-Collins laboratory liquefier.³ In this system, portions of compressed helium gas are expanded in expansion engines, following Kapitza,⁴ at intermediate temperatures to produce the refrigeration required for precooling the Joule-Thomson stream. The Collins method represents a great step towards the realization of a closed cycle refrigeration system because of its simplicity, safety, and inherent efficiency. However, there are certain problems of a practical nature inherent in the engine design which tend to limit the mechanical reliability. Foremost among these is the requirement for a closely fitting piston-cylinder combination (which, of course, cannot be lubricated), and the necessity of having mechanically operated engine valves which operate at very low temperatures.

More recently, adiabatic expansion machines of a quite different sort have been developed which could conceivably serve as precooling devices for helium liquefiers. The early concepts of Kirk and Stirling in which a reciprocating-flow thermal regenerator is used in place of a countercurrent heat exchanger have recently been refined and developed effectively into an air liquefier by the Philips Company.⁵ The system is characterized by the use of two articulated pistons which provide a compression space and an expansion space, interconnected through a thermal regenerator. Unlike the Kapitza or Collins system, there are no valves required either for the compression or expansion sections of the Philips apparatus, and this feature may be expected to be advantageous from the point of view of mechanical reliability. On the other hand, the inability to separate physically the expansion and compression sections of the machine imposes a considerable degree of inflexibility and almost eliminates the possibility of using such a refrigerator as a multi-stage precooler.

Taconis⁶ has recorded a number of ingenious ideas in the patent literature which utilize displacers and regenerators to produce refrigeration at low temperatures. These are similar in many respects to the Philips machine and also to machines which have been developed recently at Arthur D. Little, Inc.⁷⁻⁹

The most recent developments at Arthur D. Little are the results of an effort to overcome the limitations, while retaining the most attractive features, of systems utilizing thermal regenerators and displacers.

The single-stage cycle

The new refrigerator utilizes the feature of reciprocating flow through a thermal regenerator rather than steady flow through countercurrent heat exchangers. Advantages

which can be realized with thermal regenerators as compared with heat exchangers, such as extreme compactness and simplicity of construction, are thereby preserved. Unlike the Kirk-Philips cycle, however, the present refrigerator uses a conventional gas compressor with no phase co-ordination between the compression and expansion sections of the system. Another point of distinction is that mechanically controlled intake and exhaust valves, operating at room temperature, are used to control the flow of gas through the refrigerator and to define the pressure-volume cycle in a manner similar to a conventional expansion engine. A unique feature of the new refrigerator is that the expansion engine does not deliver mechanical work to the exterior; instead, it rejects enthalpy in the form of heat. The somewhat remarkable consequence of this is that the exhaust stream from the refrigerator is heated to a higher temperature than that of the entering stream.

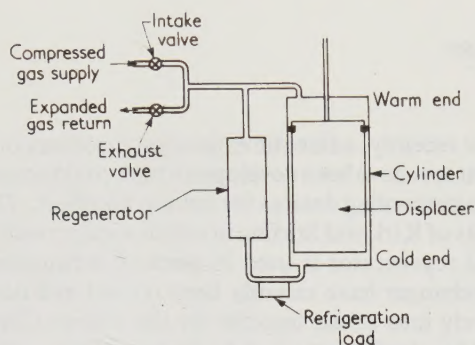


Figure 1. Single-stage refrigerator

A single-stage refrigerator utilizing the new cycle is shown schematically in Figure 1. It consists of a thin wall stainless steel cylinder into which is fitted a displacer in the form of a fairly closely fitting plastic piston which is free to move longitudinally throughout a limited distance. A rod is attached to the room temperature end of the displacer and is used to control its motion. The other end of the displacer-cylinder combination is at the low temperature. As the displacer is moved, the warm and cold volumes at the two ends of the cylinder are varied, one increasing at the expense of the other. However, these two volumes are connected together through a thermal regenerator having relatively low resistance to gas flow. Consequently, the pressure above and below the displacer is always approximately equal; and no appreciable force is required to move it.

The thermal regenerator consists of a thin wall stainless steel tube filled with circles of fine metal screen which are stacked to form a cylindrical structure just equal to the internal dimensions of the regenerator shell. The upper end of the regenerator is at approximately room temperature and the other end is at the low temperature. In spite of the large temperature gradient along the length of the regenerator, there is very little heat flow because of the poor thermal conductivity of the stacked structure.

The intake and exhaust valves, which are located at room temperature, are operated by cams attached to a crank shaft which controls the motion of the displacer. Compressed gas is supplied to the refrigerator from a more or less conventional closed cycle compression system consisting of a reciprocating two-stage compressor and the usual ballast chambers and coolers.

The cycle may be considered to be made up of four operations: *Pressurization, Intake, Expansion, and Exhaust*. At the beginning of the pressurization the displacer is at the extreme cold end of the cylinder so that the cold volume is a minimum and the warm volume is a maximum. The intake valve is opened and compressed gas rushes into the warm volume (and also the free volume of the regenerator) until the pressure is equal to that of the supply. The sudden increase of pressure in the warm volume of course causes adiabatic heating and results in a considerable temperature rise of the gas.

With the intake valve remaining open, the displacer is moved so as to enlarge the cold volume and diminish the warm volume. This displaces the heated gas through the regenerator to the cold end, causing it to decrease in volume by an amount proportional to the ratio of the absolute temperatures at the two ends. Since the intake valve is open during the operation, the pressure is constant, and more gas flows in through the intake valve and mixes with the displaced stream entering the warm end of the regenerator. At the end of the intake stroke the cold volume has reached its maximum value and is charged with cold gas at the full intake pressure. The intake valve is closed at the end of the intake stroke.

The expansion operation is carried out by opening the exhaust valve slowly over a period of time when the displacer is essentially motionless. If the expansion occurs too abruptly, poor heat transfer will result between the exhausting gas and the metal matrix of the regenerator. As expansion occurs the gas remaining in the cold volume falls to a progressively lower temperature. The gas leaving the cold volume is partially warmed by heat removal from the working temperature (the refrigeration load in Figure 1) and is subsequently heated all the way to room temperature by passage through the regenerator.

The cycle is completed by moving the displacer so as to expel the cold expanded gas remaining in the cold volume at the end of the expansion operation. The exhaust valve remains open as the displacer is lowered and is closed after the exhaust stroke is completed. The initial condition is now restored and the whole sequence of operations is repeated.

Thermodynamic considerations

Each cycle results in an enthalpy change of

$$\Delta H = +(p_1 - p_2)V$$

for the gas at the warm end of the refrigerator and a corresponding change of $\Delta H = -(p_1 - p_2)V$ at the cold end, where p_1 and p_2 are the high and low pressures, and V is the

displaceable volume. This can be demonstrated by reference to Figures 2(a) and 2(b) which show the pressure-volume diagram for a complete cycle for the warm end and cold end, respectively. The two diagrams are identical except for the fact that the p - V area is circumscribed in the anticlockwise direction at the warm end, corresponding to a reduction of enthalpy. Since all other processes involved are constant pressure processes, and since there is no mechanical work delivered, it can be concluded that, ideally, an amount of heat $(p_1 - p_2)V$ is pumped from the low temperature and rejected at room temperature for each cycle.

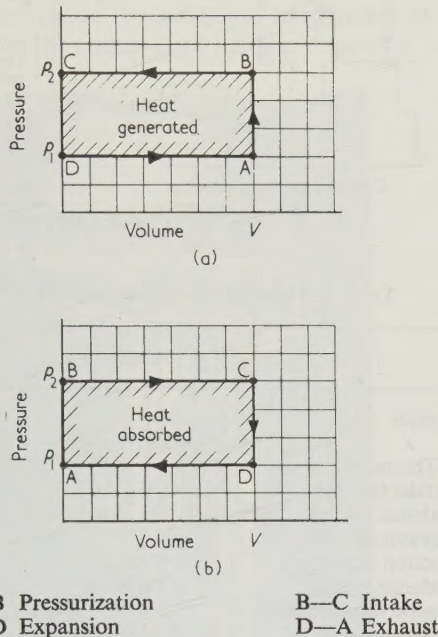


Figure 2. Pressure-volume diagrams of (a) warm volume and (b) cold volume

There are many ways in which the machine can deviate from ideal behaviour. The principal sources of inefficiency can be divided into two groups, thermal inefficiencies and pressure-volume inefficiencies. Thermal inefficiency can result from inadequate heat transfer or insufficient heat storage capacity in the thermal regenerator or at the site of the refrigeration load. Heat leakage from the warm to the cold ends of the displacer-cylinder assembly or along the regenerator also contribute to thermal inefficiency. On the other hand, poorly arranged valve timing or restricted flow passages may seriously diminish the actual pressure-volume area, thereby reducing the enthalpy change per cycle. Finally, unnecessarily large gas volumes in the flow passages or in the regenerator, valves, or connecting tubes result in gas wastage, because the static volume fills with gas and discharges each cycle without contributing to enthalpy change.

Generally speaking, minimization of thermal inefficiencies is incompatible with minimization of pressure-volume inefficiencies. For example, an ideal thermal regenerator would have extremely small flow passages, a large surface

area for good heat transfer, and a large volume of metal for good heat storage. This is clearly incompatible with the requirement of minimum internal gas volume and minimum restriction to gas flow. In order to achieve maximum efficiency for the refrigerator, it is necessary to optimize the design in multidimensional space, taking into account at least ten independent parameters. These parameters are: length and diameter of regenerator, density, specific heat and degree of subdivision of metal matrix, length and frequency of stroke, length and diameter of piston, and maximum and minimum pressure. Some of these problems have been considered in more detail in previous publications.^{7,8} An actual single-stage refrigerator shows an efficiency which is dependent on the temperature span, the efficiency decreasing as the span is increased. Several refrigerators have been constructed which produce 65–70 per cent of $(p_1 - p_2)V$ in the form of useful refrigeration, as measured by an electrical heater, at approximately 100° K, where p_1 and p_2 are 300 and 75 lb/in² above atmospheric pressure.

The multi-stage cycle

It has been noted that the efficiency of a single-stage refrigerator decreases as the temperature span increases. This suggests the possibility of using several stages arranged end-to-end in order to minimize the span covered by any single stage and thus permit the attainment of very low temperatures with high efficiency. Fortunately, the present cycle lends itself very well to this arrangement, as shown schematically in Figure 3. The operating cycle in this case is exactly the same as for the single-stage machine. Refrigeration is produced at three different temperatures: 80° K, 35° K, and 14° K in the example shown. The relative magnitudes of the displaced volumes determine the amount of refrigeration produced at each temperature and will therefore vary from one application to another.

The lowest attainable temperature at the cold end of the third stage is determined by the performance of the third-stage regenerator. The heat capacity per unit volume of all metals diminishes very rapidly at temperatures below 20° K and their heat storage ability becomes poor. The difficulty

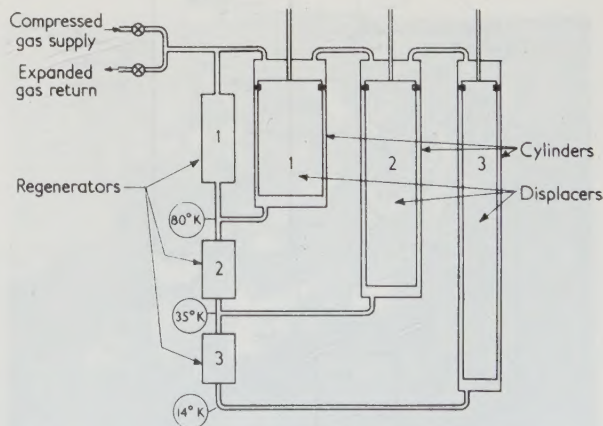


Figure 3. Three-stage refrigerator

is further aggravated by the fact that the heat capacity per unit volume of helium gas increases in inverse proportion to the temperature. As a practical matter it has been found that 13–14° K may be regarded as a lower limit if reasonable efficiency is to be preserved, although it is possible to achieve temperatures of 6–8° K if no heat load is applied.

In the multi-stage cycle, refrigeration produced at intermediate temperature levels is used for three general purposes. Firstly, it is used to make up for the inefficiency of the thermal regenerator which feeds gas to that particular temperature level. Secondly, it is used to intercept heat which is flowing into the colder zones either by conduction along the displacers and cylinders or by radiation from the warm enclosure. And finally, in the event of the machine being used as a liquefier, refrigeration at the intermediate temperatures is used to cool down that portion of gas which is actually liquefied so as to minimize the refrigeration load on the final stage.

Heat transfer between the thermal load (regardless of its origin) and the refrigeration source is established by means of heat transfer stations which form a part of the flow channels connecting the regenerators to the expansion chambers at the cold end of each cylinder. Such a heat exchanger is shown in Figure 1, but they are omitted from Figure 3 for simplicity.

The helium liquefaction cycle

A three-stage refrigerator such as is shown diagrammatically in Figure 3 can be modified by the addition of a simple Joule–Thomson cycle to achieve helium liquefaction as shown schematically in Figure 4. The Joule–Thomson stream, flowing continuously, is cooled by countercurrent flow with the unliquefied portion of gas and also by bringing it into contact with the heat transfer

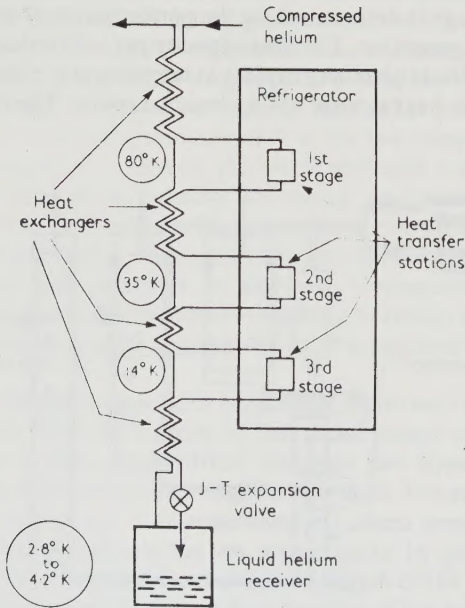


Figure 4. Helium liquefaction cycle

stations of the three-stage refrigerator at 80° K, 35° K, and 14° K. If helium gas at 300 lb/in² pressure is cooled to 14° K and expanded to 1 atm in a simple Joule–Thomson cycle, approximately 10 per cent of the gas is liquefied; the remaining 90 per cent is recirculated and recompressed. The overall recirculation system is shown in Figure 5.

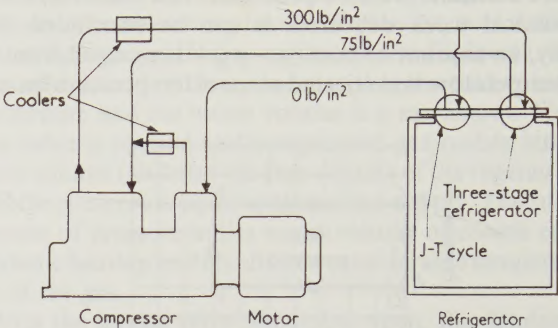


Figure 5. Helium circulation system

Table 1. Description of Helium Refrigerator

	Model 1	Model 2
Compressor		
Joule–Thomson cylinder	Water-cooled	Air-cooled
Intake (gauge)	0 lb/in ²	0 lb/in ²
Exhaust (gauge)	75 lb/in ²	75 lb/in ²
Refrigerator cylinder		
Suction (gauge)	75 lb/in ²	75 lb/in ²
Exhaust (gauge)	300 lb/in ²	300 lb/in ²
Volumetric displacement		
J–T cylinder	7.63 ft ³ /min	3.85 ft ³ /min
Refrigerator cylinder	15.30 ft ³ /min	3.85 ft ³ /min
Power consumption	10 h.p.	3 h.p.
Weight: motor and compressor	359 lb	183 lb
Size: motor and compressor	28 in. × 17½ in. × 14 in.	20 in. × 12½ in. × 12 in.
Refrigerator		
Wattage		
at 14° K	15 W	5 W
at 4.2° K	4 W	0.75 W
at 3.2° K	3 W	0.22 W
at 2.8° K	0.5 W	
Size of refrigerated space	1 ft ³	0.1 ft ³
Size of refrigerator	5 ft × 2 ft × 2 ft	27 in. × 15 in. × 9 in.
Weight of refrigerator	500 lb	90 lb
Length of		
Cylinder 1	10 in.	7 in.
Cylinder 2	20 in.	12 in.
Cylinder 3	30 in.	17 in.
Diameter of		
Cylinder 1	1½ in.	1½ in.
Cylinder 2	1½ in.	½ in.
Cylinder 3	¾ in.	¾ in.
Stroke	1 in.	1 in.
Revolution rate	75 rev/min	105 rev/min

Several closed cycle refrigeration systems have been built to date which have operated successfully at temperatures of 4.2°K and lower. While each of these experimental machines has differed from the others in some respects, they have all had certain characteristics in common. In each case the system was closed and indifferent to atmospheric pressure. The three operating pressures are established by pressure regulators which either draw gas from or deliver gas to a small storage tank permanently connected to the system. In all cases the compressors have been standard commercial Freon compressors somewhat modified for compression of helium. Special provisions have had to be made for adequate lubrication and oil separation from the compressed helium. Figures 6, 7, and

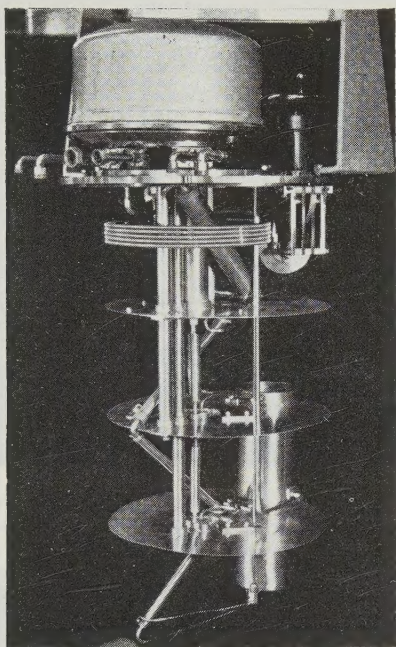


Figure 6. Internal parts of 3 W refrigerator

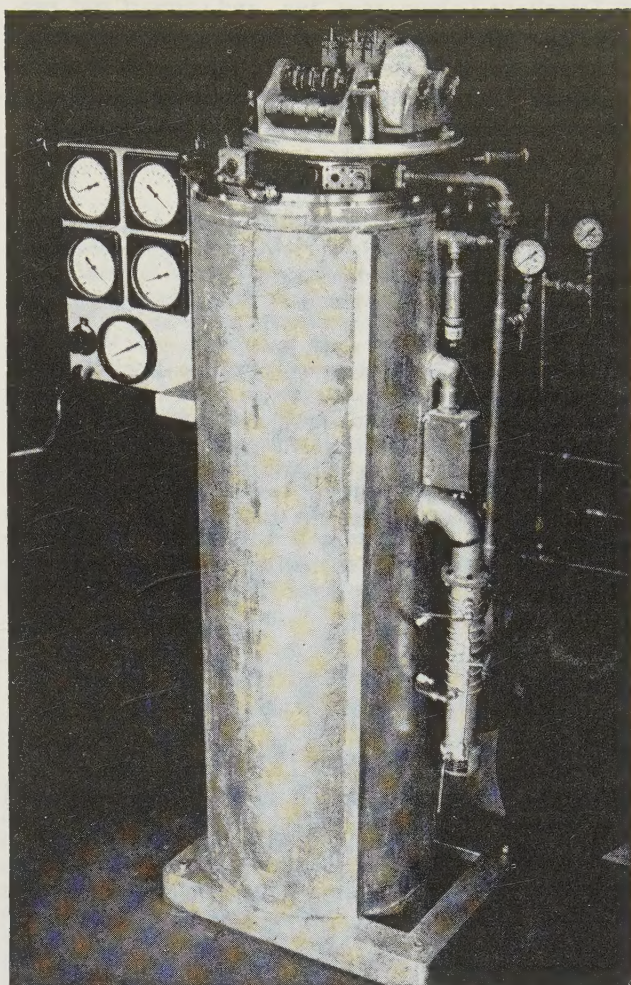


Figure 7. Complete 3 W refrigerator

8 are photographs of the refrigerator, the refrigerator in its enclosure, and the compressor system, respectively, referred to as 'Model 1' in the preceding Table. Figures 9 and 10 are photographs of 'Model 2' refrigerator and its air-cooled compressor system.

Operating experience to date has indicated that it is quite possible to run such refrigerators for periods of several hundred hours with little or no attention. Actually, the duration of a continuous operation is at present determined by the efficiency of the oil filters used on the high pressure helium supply line. Inadequate filtration of entrained oil droplets and oil vapour eventually cause clogging of the Joule-Thomson heat exchanger. It is probable that another order of magnitude improvement in reliability would require the development of compressors which do not require liquid lubricants.

Much of the work reported was sponsored by the International Business Machines Corporation and the

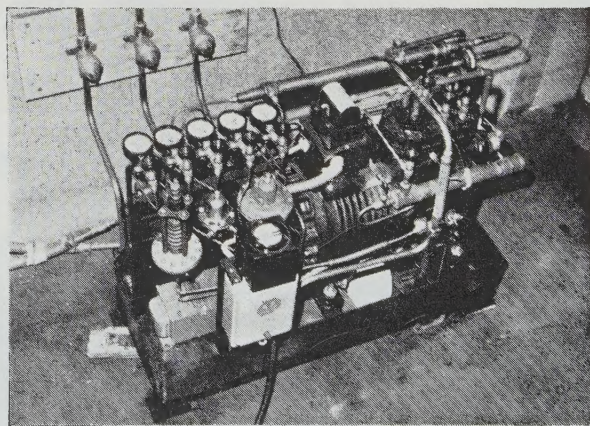


Figure 8. Compressor for 3 W refrigerator

Bell Telephone Laboratories, Inc., and support and permission to publish is gratefully acknowledged. The author also wishes to acknowledge the very great contributions of William E. Gifford and the Engineering Division of Arthur D. Little, Inc.

REFERENCES

1. ONNES, H. K. *Commun. phys. Lab. Univ. Leiden* **108**, Suppl. 21a (1908)
2. COLLINS, S. C. *Rev. sci. Instrum.* **18**, 157 (1947)
3. LATHAM, A., JR., and McMAHON, H. O. *Refrig. Engng* **57**, 549 (1949)
4. KAPITZA, P. *Proc. roy. Soc. A* **147**, 189 (1934)
5. KÖHLER, J. W. L., and JONKERS, C. D. *Philips tech. Rev.* **16**, 69 (1954)
6. TACONIS, K. W. 'Process and Apparatus for Generating Cold.' See, for example, *British Patent* 635,948 (1950)
7. McMAHON, H. O., and GIFFORD, W. E. *Advances in Cryogenic Engineering*, Vol. 5, p. 354 (1960)
8. GIFFORD, W. E., and McMAHON, H. O. *Proc. 10th Int. Congr. Refrig.* (Copenhagen, 1959)
9. GIFFORD, W. E. *Progress in Cryogenics* **3**, p. 49 (Heywood, London, 1961). In press

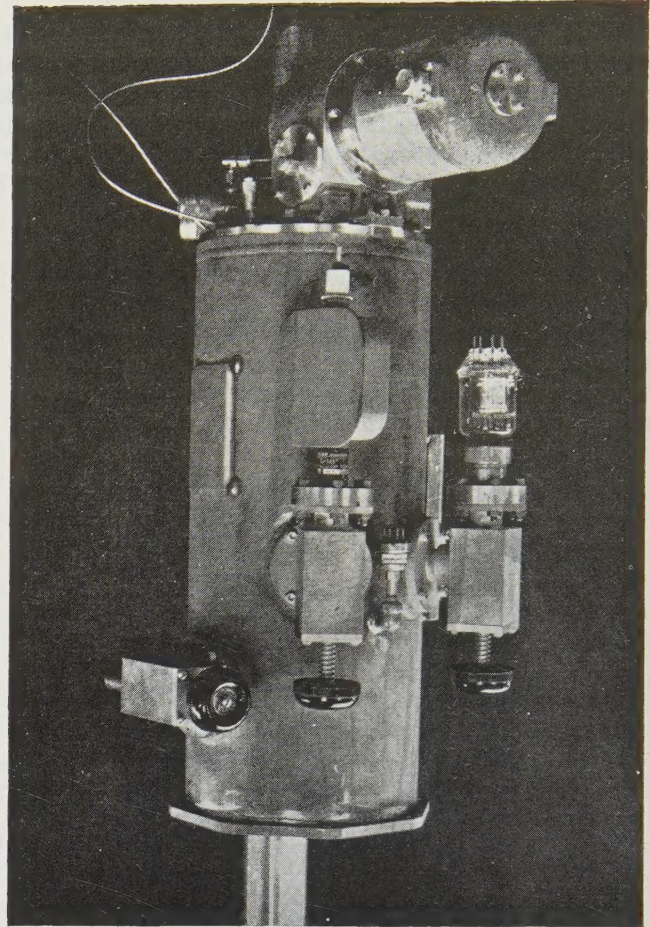
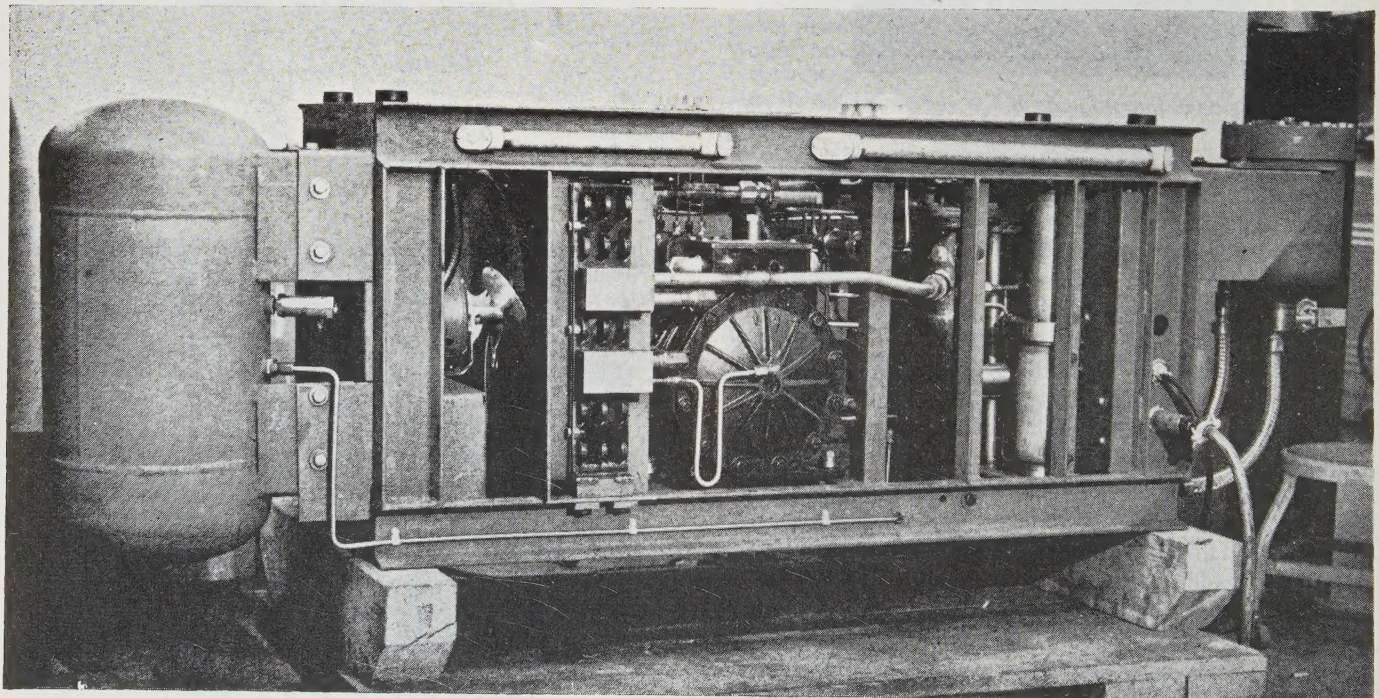


Figure 9 (right). 0.75 W refrigerator

Figure 10 (below). Compressor assembly for 0.75 W refrigerator



Abstracts

A CRYOSTAT FOR ELECTRICAL MEASUREMENTS ON SEMICONDUCTORS

B. V. ROLLIN

J. R. MILLS

J. P. RUSSELL

THE cryostat described is used for routine measurements of the resistivity and Hall coefficient of samples of semiconductors. The design enables the cryostat to be dismantled and assembled in a very short time, so that a different specimen may be measured every day. The difficulties of siphoning liquid helium have been avoided by using the transport Dewar as the experimental Dewar.

STUDIES OF THE LOW TEMPERATURE DISTILLATION OF HYDROGEN ISOTOPES

T. M. FLYNN

EXPERIMENTAL data obtained from the operation of 1.35 in. diameter distillation columns was used for the design of a pilot plant column. This column has been constructed and operated to study the separation of hydrogen deuteride from hydrogen by fractional distillation.

The pilot plant column contains thirty plates 6 in. in diameter made of 40 mesh screen, and has a maximum feed rate of 14.2 ft³(n.t.p.)/min. The column was operated with vapour velocities ranging from 0.2 to 2.0 in./sec, and reflux ratios from total to an (L/D) of 2.05. Overall plate efficiencies were investigated and found to vary, as a function of vapour velocity, from 45 to 55 per cent.

The overall plate efficiencies of the pilot plant column are significantly lower than those of the smaller diameter columns. This difference in plate efficiency is examined theoretically. A model considering the effect of liquid mixing on the plate satisfactorily describes the change in efficiency and predicts that no further decrease in efficiency with increasing diameter will occur.

DENSITY OF LIQUID OXYGEN AS A FUNCTION OF PRESSURE AND TEMPERATURE

A. VAN ITTERBEEK

O. VERBEKE

A DESCRIPTION is given of an apparatus for measuring the density of liquefied gases as a function of pressure. Experimental results of the density of liquid oxygen as a function of temperature and pressure are given from 90° K to 65° K and up to 150 kg/cm². Some thermodynamic properties, such as γ , the Poisson's ratio, and W , the velocity of sound, are calculated. A comparison with the existing measurements of these thermodynamic functions is made.

COOLING BY ADIABATIC MAGNETIZATION OF SUPERCONDUCTORS

M. YAQUB

IN order to develop a method of attaining temperatures below 1° K, a cryostat has been designed to investigate the fall in temperature on magnetizing superconductors. It is found that by magnetizing a cylindrical specimen of pure tin from an initial temperature of 0.9° K, the lowest temperature which can be reached is 0.35° K. This is substantially higher than the expected value of 0.02° K for ideal cooling. Magnetizations have also been performed on tin-indium alloys. The lowest temperatures obtained with 0.5, 1.0, and 2.0 per cent alloys are 0.19, 0.18, and 0.345° K, respectively. It has been shown that the time taken to warm from 0.35° K, the lowest temperature attained with pure tin, can be as long as six hours. The causes of irreversibility, supported by indirect evidence, have been discussed.

A LOW TEMPERATURE PLANT FOR THE PRODUCTION OF HEAVY WATER

J. HÄNNY

THE article describes a plant for the production of heavy water (D₂O) which has been erected by Sulzer Brothers for Emser Werke AG, at Domat/Ems, Switzerland. The raw material is natural water which first undergoes seven-fold deuterium enrichment in three electrolysis stages. The gaseous mixture of hydrogen and deuterium produced by electrolytic dissociation is cooled to -250° C and thereby liquefied. The liquid then goes to a Kuhn rectifying column where the exchange processes taking place at 23° K result in 400-fold deuterium enrichment. The product of the column is burnt with oxygen and is thereupon passed to a second Kuhn column in which the heavy water concentration is brought up to 99.8 per cent. It is the only known plant for the liquefaction of hydrogen which utilizes expansion turbines only, without any preliminary nitrogen cooling.

SUPERFLUIDITY AND SPECIFIC HEAT OF LIQUID HELIUM IN 'VYCOR' POROUS GLASS

D. F. BREWER D. C. CHAMPENEY K. MENDELSSOHN

THE flow rate of liquid helium through disks of 'Vycor' porous glass has been measured as a function of temperature at constant pressure head. The specific heat of liquid helium within the same disks has also been measured. The mean pore diameter as given by adsorption measurements was 71 Å, and the onset of superfluidity and the specific heat maximum occurred, respectively, at $2.0 \pm 0.1^\circ$ K and at 2.06° K. The effect of pore size distribution is discussed, and the results compared with similar measurements using the unsaturated helium-II film.

THE CRITICAL FIELD OF SUPERCONDUCTING ALUMINIUM UNDER PRESSURE

D. GROSS

J. L. OLSEN

THE effect of pressure p on the critical field H_c of aluminium has been measured between 0.3° K and the transition temperature T_c . Pressures up to about 1,700 atm were made by the ice-bomb technique. We find

$$\partial H_c / \partial p = -[3.1 \pm 0.2 + (1.7 \pm 0.2)(T/T_c)^2] \times 10^{-9} \text{ gauss dyn}^{-1} \text{ cm}^2$$

This yields

$$(d \ln \gamma) / (d \ln v) = 8 \pm 4$$

where γT is the electronic specific heat per mole. Results on zinc are also reported. Here $\partial H_c / \partial p$ appears to be anisotropic.

DISCUSSION ON ENTHALPIES OF MIXTURES

M. RUHEMANN

COMMISSION I of the International Institute of Refrigeration, meeting at Eindhoven in June, 1960, devoted a session to the lack of information on the enthalpies of gaseous and liquid mixtures, under the chairmanship of the author. A short report is given here.

Résumés

CRYOSTAT POUR MESURES ELECTRIQUES SUR LES SEMICONDUCTEURS

B. V. ROLLIN

J. R. MILLS

J. P. RUSSELL

Le cryostat décrit est utilisé pour les mesures de la résistivité et du coefficient Hall d'échantillons de semiconducteurs. La construction permet de démonter et d'assembler le cryostat en un temps très court, ce qui permet de mesurer chaque jour un spécimen différent. Les difficultés de transvasement de l'hélium liquide par siphon ont été évitées en employant le Dewar de transport comme Dewar expérimental.

DENSITE DE L'OXYGENE LIQUIDE EN FONCTION DE LA PRESSION ET DE LA TEMPERATURE

A. VAN ITTERBEEK

O. VERBEKE

UNE description est donnée d'un appareil permettant de mesurer la densité de gaz liquéfiés en fonction de la pression. Des résultats d'expérience sont donnés pour la densité de l'oxygène liquide en fonction de la température et de la pression entre 90° K et 65° K et jusqu'à 150 kg cm². Certaines propriétés thermodynamiques sont calculées, telles que γ , le rapport de Poisson, et W , la vitesse du son. Une comparaison est faite avec les mesures existantes de ces fonctions thermodynamiques.

UNE INSTALLATION POUR LA PRODUCTION D'EAU LOURDE A BASSE TEMPERATURE

J. HÄNNY

L'ARTICLE qui suit décrit une installation pour la production d'eau lourde (D₂O), établie par Sulzer Frères dans les usines d'Ems, à Domat Ems (Suisse). La matière première est l'eau naturelle, enrichie sept fois en deutérium par trois phases d'électrolyse. Le mélange gazeux d'hydrogène et de deutérium, provenant de la décomposition électrolytique, est refroidi à -250 C et liquéfié, puis ce liquide passe dans une colonne à rectifier Kuhn, où l'opération d'échange à 23 K enrichit de 400 fois la teneur en deutérium. Le produit ainsi obtenu est brûlé avec de l'oxygène puis concentré dans une seconde colonne Kuhn, pour laisser en fin de compte de l'eau lourde à 99,8 pour cent. C'est à notre connaissance la seule installation dans laquelle on n'applique que des turbines de détente, sans aucun refroidissement préliminaire de l'azote.

LE CHAMP CRITIQUE DE L'ALUMINIUM SUPRACONDUCTEUR SOUS PRESSION

D. GROSS

J. L. OLSEN

L'EFFET d'une pression p sur le champ critique H_c de l'aluminium a été mesuré entre 0,3 K et la température de transition T_c . Des pressions allant jusqu'à environ 1.700 atmosphères ont été réalisées au moyen de la technique de la 'bombe à glace'. On constate que $\partial H_c / \partial p = -[3,1 \pm 0,2 + (1,7 \pm 0,2)(T/T_c)^2] \times 10^{-9}$ gauss dyne⁻¹ cm² ce qui donne

$$(d \ln \gamma) / (d \ln v) = 8 \pm 4$$

γT étant la chaleur spécifique électronique par mole. On donne également les résultats relatifs au zinc. Dans ce cas, $\partial H_c / \partial p$ semble être anisotrope.

ETUDES DE LA DISTILLATION A BASSE TEMPERATURE DES ISOTOPES D'HYDROGENE

T. M. FLYNN

LES données expérimentales obtenues au cours du fonctionnement de colonnes de distillation de 1,35 in. de diamètre ont servi à l'étude

d'une colonne pour installation pilote. Cette colonne a été construite et utilisée pour l'étude de la séparation de HD et H₂ par distillation fractionnée.

La colonne de l'installation pilote est constituée de trente plateaux de 6 in. de diamètre, faits de toile à tamis à 40 mailles par pouce; le taux d'alimentation maximum est de 14,2 ft³ par minute. La colonne fonctionne avec des vitesses de vapeur allant de 0,2 à 2,0 in./sec et des taux de reflux variant d'un reflux total à un (L/D) de 2,05. L'efficacité moyenne des plateaux a été étudiée et on a constaté qu'elle varie, en fonction de la vitesse de la vapeur, de 45 à 55 pour cent.

L'efficacité moyenne des plateaux de la colonne de l'installation pilote est nettement inférieure à celle des colonnes de diamètres plus faibles. L'auteur examine, d'un point de vue théorique, cette différence dans l'efficacité des plateaux. Un modèle tenant compte de l'effet du brassage du liquide sur les plateaux permet de rendre compte de façon satisfaisante du changement d'efficacité et de prévoir qu'une augmentation du diamètre ne déterminera pas une nouvelle réduction de l'efficacité.

REFROIDISSEMENT PAR L'AIMANTATION ADIABATIQUE DES SUPRACONDUCTEURS

M. YAQUB

POUR mettre au point une méthode qui permettra d'atteindre des températures inférieures à 1° K, on a conçu et construit un cryostat pour l'étude de l'abaissement de température qui accompagne l'aimantation des supraconducteurs. On a constaté que la température la plus basse qu'on puisse atteindre en aimantant un échantillon cylindrique d'étain pur à partir d'une température initiale de 0,9° K, est de 0,35° K. On espérait atteindre 0,02° K, pour le refroidissement idéal, et la température obtenue est évidemment bien plus élevée. On a également aimanté des alliages d'étain et d'indium. Les températures les plus faibles que l'on ait réussi à atteindre, avec des alliages à 0,5, 1 et 2 pour cent ont été de 0,19, 0,18 et 0,345° K respectivement. On a montré que le temps nécessaire pour le réchauffage, à partir de 0,35 K, la température la plus basse atteinte avec l'étain pur, peut aller jusqu'à six heures. L'auteur examine les causes de l'irréversibilité, en s'appuyant sur des renseignements indirectes.

SUPERFLUIDITE ET CHALEUR SPECIFIQUE DE L'HELIUM LIQUIDE DANS UN VERRE POREUX 'VYCOR'

D. F. BREWER D. C. CHAMPENEY K. MENDELSSOHN

ON a mesuré l'écoulement de l'hélium liquide à travers des disques de verre poreux 'Vycor' en fonction de la température, sous une surpression constante. On a également mesuré la chaleur spécifique de l'hélium liquide dans ces mêmes disques. Le diamètre moyen des pores, donné par des mesures d'adsorption, était de 71 Å; la superfluidité apparaissait à $2,0 \pm 0,1$ K et la chaleur spécifique passait par un maximum à 2,06° K. Les auteurs examinent l'influence de la répartition en dimension des pores et comparent les résultats à ceux des mesures semblables faites avec un film d'hélium-II non saturé.

DEBAT SUR LES ENTHALPIES DES MELANGES

M. RUHEMANN

LA COMMISSION I de l'Institut International de Réfrigération, réunie à Eindhoven, en juin 1960, a consacré toute une séance au manque de renseignements sur les enthalpies des mélanges gazeux et liquides. L'auteur, qui a présidé cette séance, donne, ici, un bref compte rendu de la discussion.

Auszüge

EIN TIEFTEMPERATURGERÄT FÜR ELEKTRISCHE MESSUNGEN AN HALBLEITERN

B. V. ROLLIN J. R. MILLS J. P. RUSSELL

Das hier beschriebene Tieftemperaturgerät dient zu Routinemessungen des spezifischen Widerstandes und des Hall-Koeffizienten von Halbleiterproben. Das Gerät ist so konstruiert, dass es sehr schnell auseinandergenommen oder zusammengesetzt werden kann, so dass täglich eine andere Probe gemessen werden kann. Die sich beim Überhebern von Helium ergebenden Schwierigkeiten wurden durch Benutzung des Transportdewargefäßes als Messgefäß überwunden.

DICHTE DES FLÜSSIGEN SAUERSTOFFS ALS FUNKTION VON DRUCK UND TEMPERATUR

A. VAN ITTERBEEK O. VERBEKE

Beschreibung eines Gerätes zur Messung der Dichte verflüssigter Gase in Abhängigkeit vom Druck. Die Dichte des flüssigen Sauerstoffs wurde zwischen 90° K und 65° K und bis zu 150 kg/cm² als Funktion der Temperatur und des Druckes bestimmt. Einige thermodynamische Eigenschaften wie z.B. γ , das Poissonsche Verhältnis, und W , die Schallgeschwindigkeit, wurden berechnet und mit früheren Werten dieser thermodynamischen Funktionen verglichen.

EINE TIEFTEMPERATURANLAGE ZUR HERSTELLUNG VON SCHWEREN WASSER

J. HÄNNY

Die folgenden Ausführungen beschreiben eine Anlage zur Gewinnung von schweren Wasser, welche in den 'Emser Werken AG' in Domat/Ems steht und von Gebrüder Sulzer hergestellt wurde. Als Ausgangsprodukt dient natürliches Wasser, das sich in drei Elektrolyseurstufen siebenfach an Deuterium anreichert. Das bei der elektrolytischen Zerlegung entstehende gasförmige Wasserstoff-Deuterium-Gemisch wird auf -250°C abgekühlt und verflüssigt. Anschließend gelangt die Flüssigkeit in eine Kuhn-Rektifizierkolonne, wo der Austauschvorgang bei 23° K eine vierhundertfache Deuteriumanreicherung bewirkt. Das gewonnene Produkt wird mit Sauerstoff verbrannt und in einer zweiten Kuhn-Kolonne zu 99,8 prozentigem schwerem Wasser aufkonzentriert. Es ist die einzige heute bekannte Anlage zur Verflüssigung von Wasserstoff, welche nur Expansionsturbinen und keine Stickstoffvorkühlung benötigt.

DIE KRITISCHE FELDESTÄRKE VON UNTER DRUCK STEHENDEN ALUMINIUM-SUPRALEITERN

D. GROSS J. L. OLSEN

Der Effekt des Drucks p auf die kritische Feldstärke H_c von Aluminium wurde zwischen 0,3° K und der Übergangstemperatur T_c gemessen. Drücke bis zu 1700 atm. wurden mittels der Eisbombenmethode hergestellt. Es ergab sich

$$\partial H_c / \partial p = -[3,1 \pm 0,2 + (1,7 \pm 0,2) (T/T_c)^2] \times 10^{-9} \text{ gauss dyn}^{-1} \text{ cm}^2$$

und daraus

$$(d \ln \gamma) / (d \ln v) = 8 \pm 4$$

worin γT die spezifische Elektronenwärme pro Mol ist. Ergebnisse mit Zink werden ebenfalls besprochen, wobei $\partial H_c / \partial p$ anisotropisch zu sein scheint.

TIEFTEMPERATURDESTILLATION VON WASSERSTOFFISOTOPEN

T. M. FLYNN

Versuchswerte, die im Betrieb mit einer Destillationssäule von 1,35 in. Durchmesser erzielt wurden, sind für die Bemessung einer Versuchskolonnen verwertet worden. Diese Kolonne wurde gebaut und betrieben, um die Trennung von Wasserstoffdeuterid und Wasserstoff durch fraktionierte Destillation zu studieren.

Die Versuchsanlage enthält dreissig Böden von 6 in. Durchmesser aus 40-er Maschensieb und hat eine maximale Zuflussmenge von 14,2 ft³/min. Die Kolonne wurde mit Dampfgeschwindigkeiten von 0,2 bis 2,0 in./sec und mit Rückflussverhältnissen von unendlich bis zu (F/E) von 2,05 betrieben. Messungen des Verstärkungsverhältnisses ergaben Schwankungen als Funktion der Dampfgeschwindigkeit zwischen 45 und 55%.

Das Verstärkungsverhältnis der Versuchsanlage war bedeutend niedriger als dasjenige von Kolonnen mit kleinerem Durchmesser. Dieser Unterschied im Verstärkungsverhältnis wird theoretisch untersucht. Ein die Wirkung der Flüssigkeitsmischung auf dem Boden veranschaulichendes Modell beschreibt die zufriedenstellend die Änderung des Verstärkungsverhältnisses und lässt darauf schliessen, dass bei noch grösseren Durchmessern keine weitere Abnahme stattfinden wird.

KÜHLUNG DURCH ADIABATISCHE MAGNETISIERUNG VON SUPRALEITERN

M. YAQUB

Um ein Verfahren zur Erreichung von Temperaturen unter 1° K zu entwickeln wurde ein Kälte-regler entworfen, der den Temperaturabfall bei der Magnetisierung von Supraleitern zu studieren gestattet. Es wurde gefunden, dass durch Magnetisierung eines Zylinders aus reinem Zinn bei einer Ausgangstemperatur von 0,9° K eine tiefste Temperatur von 0,35° K erreicht werden kann. Diese ist bedeutend höher, als der bei idealer Kühlung erwartete Wert von 0,02° K. Magnetisierungsversuche wurden auch mit Zinn-Indium-Legierungen durchgeführt. Die tiefsten Temperaturen, die mit 0,5%, 1,0% und 2,0% Legierungen erzielt wurden, sind 0,19, 0,18, bzw. 0,345° K. Es hat sich gezeigt, dass die Aufwärmzeit von 0,35° K, d.h., von der tiefsten mit reinem Zinn erreichten Temperatur, bis zu sechs Stunden betragen kann. Die Ursachen der Irreversibilität, die durch indirekte Beweise gestützt sind, wurden besprochen.

SUPRAFLUIDITÄT UND SPEZIFISCHE WÄRME VON FLÜSSIGEM HELIUM IN PORÖSEM 'VYCOR' GLAS

D. F. BREWER D. C. CHAMPENY K. MENDELSSOHN

Die Durchflussleistung von flüssigem Helium durch poröse 'Vycor' Glas-Platten wurde als Funktion der Temperatur bei konstanter Druckhöhe gemessen. Die spezifische Wärme von flüssigem Helium innerhalb derselben Platten wurde ebenfalls gemessen. Der durch Adsorptionsmessungen bestimmte durchschnittliche Porendurchmesser ergab sich zu 71 Å. Der Beginn der Suprafluidität, bzw. das Maximum der spezifischen Wärme, traten bei $2,0 \pm 0,1$ ° K und bei 2,06° K ein. Der Einfluss der Verteilung der Porengrossen wird besprochen, und das Resultat wird mit ähnlichen Messungen verglichen, die mit ungesättigtem Helium-II-Film erhalten wurden.

AUSSPRACHE ÜBER DIE ENTHALPIEN VON GEMISCHEN

M. RUHEMANN

Die I. Kommission des Internationalen Kälte-Instituts hat sich in ihrer Sitzung in Eindhoven im Juni 1960 unter dem Vorsitz des Verfassers mit den unzureichenden Kenntnissen der Enthalpien von Gas- und Flüssigkeitsgemischen befasst. Der Verfasser erstattet einen kurzen Bericht.

Резюме

КРИОСТАТ ДЛЯ ЭЛЕКТРИЧЕСКИХ ИЗМЕРЕНИЙ ПОЛУПРОВОДНИКОВ

B. V. ROLLIN

J. R. MILLS

J. P. RUSSELL

Описанный криостат употребляется для очередных измерений удельного сопротивления и коэффициента Холла образцов полупроводников. Благодаря его конструкции криостат можно разобрать и собрать в течение очень короткого времени, так что ежедневно можно измерять разные образцы. Пользованием транспортным дюаром вместо экспериментального дюара можно избежать трудности сифонирования жидкого гелия.

ПЛОТНОСТЬ ЖИДКОГО КИСЛОРОДА КАК ФУНКЦИЯ ДАВЛЕНИЯ И ТЕМПЕРАТУРЫ

A. VAN ITTERBEEK

O. VERBEKE

Дается описание аппарата для измерения плотности разжиженных газов как функция давления. Даются экспериментальные результаты о плотности жидкого кислорода как функция температуры и давления от 90° К до 65° К и до 150 кг/см². Вычислены некоторые термодинамические свойства, как например γ , отношение Пуассона и W , скорость звука. Эти термодинамические функции сравниваются с существующими измерениями.

НИЗКОТЕМПЕРАТУРНАЯ УСТАНОВКА ДЛЯ ПРОИЗВОДСТВА ТЯЖЕЛОЙ ВОДЫ

J. HÄNNY

В статье описывается установка для производства тяжелой воды (D₂O), которая установлена фирмой Сулцер (Sulzer Brothers) для фирмы Эмсер Верке АГ (Emser Werke AG) у Домат/Эмс в Швейцарии. Сырьем служит природная вода, которая сперва подвергается семикратному обогащению относительно дейтерия в трёх ступенях электролиза. Газовая смесь водорода-дейтерия, произведенная электролитической диссоциацией, охлаждается до -250° С и так ожижается. Потом жидкость приводится в ректификационную колонну типа Кун, в которой достается 400-кратное обогащение относительного дейтерия путём обменных процессов при 23° К. Продукт образованный в колонне сжигается при кислороде и затем приводится в другую колонну типа Кун, в которой концентрация тяжелой воды увеличивается до 99,8%. Описываемая станция является единственной установкой для ожижения водорода на которой применяются только турбины с расширением пара без предварительного охлаждения азотом.

КРИТИЧЕСКОЕ ПОЛЕ СВЕРХПРОВОДЯЩЕГО АЛЮМИНИЯ ПОД ДАВЛЕНИЕМ

D. GROSS

J. L. OLSEN

Влияние давления p на критическое поле H_c алюминия было определено при температурах между 0,3° К и переходной температурой T_c . Ледяная бомба была применена для создания давлений до 1.700 ат. Находим

$$\partial H_c / \partial p = -[3,1 \pm 0,2 + (1,7 \pm 0,2) (T/T_c)^2] \times 10^{-9} \text{ гаусс дина}^{-1} \text{ см}^2$$

Это дает

$$(d \ln \gamma) / (d \ln v) = 8 \pm 4$$

где γT — электронная удельная теплота на грамм-молекулу. Результаты для цинка тоже докладываются. В этом же случае $\partial H_c / \partial p$ кажется анизотропным.

ИЗУЧЕНИЯ НИЗКОТЕМПЕРАТУРНОЙ ДИСТИЛЛЯЦИИ ВОДОРОДНЫХ ИЗОТОПОВ

T. H. FLYNN

Опытные данные, полученные от работы дистиляционных колонок диаметром 1,35 дюйма, применились для конструкции полувзаводской колонны. Эта колонна построена и приведена в действие для изучения выделения дейтерида водорода из водорода путем фракционированной дистиляции.

Полувзаводская колонна содержит тридцать тарелок диаметром 6 дюймов, сделанных из сит 40 отверстий; максимальная скорость питания — 14,2 футов³ (н.т.д.) в минуту. Колонна работала при скоростях пара от 0,2 до 2,0 дюйма в секунду и при числах флегмы (жидкость/дистиллат) от полноты до 2,05. Общие эффективности тарелок были исследованы; находилось что они изменяются, как функция скорости пара, от 45 до 55%.

Общие коэффициенты полезного действия тарелок полувзаводской колонны значительно ниже чем к.п.д. тарелок колонок меньших диаметров. Эта разница между к.п.д. тарелок исследуется теоретически. Модель, по которой учитывается влияние смешивания жидкости на тарелку, показывает изменение к.п.д. удовлетворительно и предсказывает что большего уменьшения к.п.д. не будет при увеличении диаметра.

ОХЛАЖДЕНИЕ ПО МЕТОДУ АДИАБАТИЧЕСКОЙ МАГНЕТИЗАЦИИ СВЕРХПРОВОДНИКОВ

M. YAQUB

Чтобы развивать метод достижения температур ниже 1° К, сконструирован криостат для исследования снижения температуры при магнетизации сверхпроводников. Находится что при магнетизации цилиндрического образца чистого олова от исходной температуры 0,9° К нисшая достигаемая температура — 0,35° К; эта температура существенно выше ожидаемой температуры 0,02° К при идеальном охлаждении. Выполнены тоже магнетизации сплавов олово-индий. При сплавах 0,5%, 1,0% и 2,0% соответственные нисшие достигнутые температуры — 0,19° К, 0,18° К и 0,345° К. Показывается что срок нагревания от 0,35° К, нисшей температуры достигнутой при чистого олова, может удлиниться до шести часов. Обсуждается причины необратимости, с помощью непрямого доказательства.

СВЕРХТЕКУЧЕСТЬ И ТЕПЛОЕМКОСТЬ ЖИДКОГО ГЕЛИЯ В ПОРИСТОМ СТЕКЛЕ «ВИКОР»

D. F. BREWER D. C. CHAMPENEY K. MENDELSSOHN

Измерилась скорость течения жидкого гелия через диски пористого стекла «Викор» как функция температуры при постоянном давлении. Измерилась также теплоемкость жидкого гелия в тех же самых дисках. Средний диаметр пор, определённый измерениями адсорбции, составлял 71 Å, и начало сверхтекучести и максимальная теплоемкость находились при $2,0 \pm 0,1$ ° К и при 2,06° К соответственно. Обсуждается влияние распределения размеров пор, и результаты сравниваются с подобными измерениями, полученными путём применения ненасыщенной пленки гелия—II.

ОБСУЖДЕНИЕ ЭНТАЛЬПИЙ СМЕСЕЙ

M. RUHEMANN

Комиссия I Международного Института по Охлаждению, состоявшаяся в Эйндговене (в Голландии) в июне 1960 г., отдала сессию обсуждению вопроса недостатка информации по поводу энтальпий газовых и жидких смесей, под председательством автора. Здесь представлен краткий доклад.

A Cryostat for Electrical Measurements on Semiconductors

B. V. Rollin, J. R. Mills, and J. P. Russell *Clarendon Laboratory, Oxford*

Received 17 May 1960

A FUNDAMENTAL factor in research on semiconductors is a knowledge of the concentrations of acceptor and donor impurities, and of the activation energy associated with these. The usual way of discovering this is to investigate the variation of the resistivity and the Hall coefficient with temperature between liquid helium temperature and room temperature. The cryostat described enables temperatures between 4.2°K and 1.5°K to be obtained by lowering the vapour pressure above the helium bath, and temperatures above 4.2°K to be obtained by evacuating the space round the vessel containing the specimen, and passing current through a heater.

One of the major difficulties in the use of liquid helium is the transfer of the liquid from one Dewar to another, particularly since the cost of helium makes it necessary to save all the evaporated gas. In most installations two transfer operations are necessary; first from the storage container into a transport Dewar and then from the transport Dewar into the cryostat. In the present design the second operation has been eliminated by enabling the transport Dewar to be put on to the cryostat and to be used as the experimental Dewar. Loss of gas during this operation is prevented by a sliding seal (clearance, 0.001 in.) between a brass sleeve A and a long thin-walled german silver tube B forming the outer casing.

As materials such as germanium and silicon may have a resistivity greater than $10^{10}\ \Omega\text{cm}$ at low temperatures, special precautions have been taken in insulating the leads, in the electrical screening, and in avoidance of frictional charges which can be produced by the boiling liquid helium shaking the polythene sleeving encasing the leads. This is prevented by enclosing the leads in the tube B so that they are not in contact with the liquid helium. The specimens may be sensitive to long wavelength infra-red radiation from the warmer parts of the apparatus and must be shielded. Surface contamination and physical strains must be reduced to a minimum.¹

The specimen is a bar $1.5\text{ cm} \times 0.3\text{ cm} \times 0.1\text{ cm}$ cut from a single crystal ingot, with six contacts enabling the resistivity and Hall coefficient to be measured using a transverse magnetic field. This specimen is suspended from the mount by its electrical leads only, so that there is no straining or contamination. The mount is based on a modified B7G valve-holder which fits a standard 8-pin metal-glass seal, opaque to infra-red radiation, forming the top of a small thin-walled brass can C containing the specimen. The can C, which can be dismantled at a Wood's

metal joint, is filled with helium gas and is connected to a manometer by 1 mm german silver capillary, thus acting as a simple gas thermometer. A carbon resistance thermometer is fixed to the bottom of the can C and is used as a secondary thermometer.

The long german silver tube B forms a vacuum space in which the can C is suspended by thin german silver supports. Heat leakage down the leads has been reduced by cementing them to Perspex spacers which are attached to copper rings making thermal contact with B by means of the springs D. Copper shields reduce the thermal radiation down the tube. A piece of 35 s.w.g. constantan wire attached to the bottom of the can C presses against the bottom of B forming a small heat leak enabling the temperature of C to be controlled more readily. At the

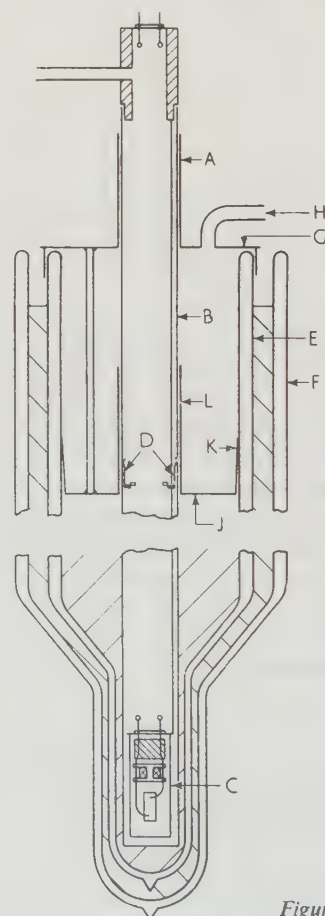


Figure 1. The cryostat

top of the cryostat are two standard 7-pin metal-glass seals for the electrical connections.

The liquid helium is contained in a silvered glass Dewar E of normal design, surrounded by liquid oxygen in a second Dewar F, both having narrow tails to fit an electromagnet. The inner Dewar is closed by a brass top G (made gas-tight by rubber), to which the sleeve A is attached. Evaporated helium gas escapes through the tube H and is collected in a balloon pending return to the liquefier. Radiation downwards into the liquid helium is reduced by the silver-plated brass shield J which is cooled by the evaporated gas. A spring skirt K round the edge of the shield forces most of the gas to flow between the tubes L and B, assisting in the cooling of both B and J which reach a steady temperature of about 120° K.

Procedure

The cryostat is first of all assembled: the specimen is soldered on to the mount which is plugged on to the 8-pin seal, the can C is soldered together, the tube B is pushed up over the springs D and is sealed by a Wood's metal joint. The air is now pumped out of both the can C and the tube B; C is filled with helium to a pressure of about 30 cm, B with about 1 mm helium exchange gas.

The inner Dewar is pre-cooled with liquid oxygen (the liquid oxygen being carefully emptied out again), and put into the outer Dewar which is then filled with liquid oxygen. The required amount of liquid helium is then siphoned from the storage vessel into the inner Dewar. The Dewars are now positioned under the cryostat, a flexible return line is attached, and the Dewars are raised until the bottom of the tube B is just inside the tube L. The evaporating gas cools the specimen to about 150° K in 5 min. The Dewars are now lifted into their final position. It is very important that this should be done slowly as the tube B is then cooled efficiently by the evaporating gas and a minimum of liquid helium is used in cooling the apparatus to its final temperature. With 1 l. of liquid helium the Dewars should be raised 1 in. every minute, and about 70 cm³ of liquid helium evaporate by the time the Dewars are in the final position. When in the final position a support on the sleeve A is put into a clamp, the outer Dewar is attached to a supporting ring by springs, a piece of rubber is slipped over the top of the sleeve A and wired on to make it vacuum-tight, and the flexible return line is replaced by a metal pipe suitable for pumping.

Associated equipment

The cryostat has the usual high vacuum system, and a pump for lowering the vapour pressure of the helium bath. The electrical measurements are made with a vibrating reed electrometer in conjunction with a simple switching system enabling the voltage across the two potential contacts, the Hall contacts, or a comparable series resistance to be observed. The system is insulated throughout with polythene or polystyrene. Specimen

resistances up to $4 \times 10^{11} \Omega$ can be measured and at this resistance Hall voltages of the order of millivolts can be observed.

The carbon resistance thermometer with a heat dissipation of less than 10^{-7} W forms one arm of a Wheatstone bridge provided with compensating leads running to the bottom of the cryostat. A galvanometer amplifier is used to indicate balance and the d.c. output of this amplifier is further amplified by a d.c. transistor amplifier. The output of this amplifier is passed through the heater and automatically controls the temperature. This arrangement enables the temperature to be held steady to within ± 0.2 per cent, which is very necessary because of the rapid variation with temperature of the properties being observed.

Performance of apparatus

Time required for assembly and initial cooling	1–1.5 hr
Volume of liquid helium evaporated during initial cooling	70 cm ³
Evaporation rate of liquid helium	1 cm ³ /min
Average duration of experiment using 1 l. of liquid helium	10 hr
Accuracy of temperature measurement:	
Gas thermometer	± 2 per cent
Resistance thermometer	± 5 per cent
Temperature stability using amplifier described	± 0.2 per cent
Minimum temperature obtainable (Using liquid hydrogen)	1.5° K (10.8° K)
Maximum temperature obtainable	290° K
Leakage resistance	$10^{13} \Omega$
Maximum resistance observable	$4 \times 10^{11} \Omega$
Minimum Hall voltage observable	
At low resistance	0.2 mV
At high resistance	2 mV

Principal dimensions

Length of tube B	80 cm
Diameter of tube B	3 cm
Wall thickness of tube B	0.4 mm
Maximum capacity of inner Dewar	1.75 l.

Acknowledgements

The Authors are indebted to Mr. J. M. Rowell who demonstrated the possibility of this method of cooling with liquid helium with an apparatus for photoconductivity measurements over a similar temperature range.

This work has been assisted by an Admiralty Research Contract, by a D.S.I.R. Research Studentship (J. R. M.) and by a Research Studentship from the Ministry of Education of Northern Ireland (J. P. R.)

REFERENCE

1. FRITZSCHE, H., and LARK-HOROVITZ, K. *Physica* **20**, 834 (1954)

Density of Liquid Oxygen as a Function of Pressure and Temperature

A. Van Itterbeek and O. Verbeke

Instituut voor Lage Temperaturen en Technische Fysika, Leuven, Belgium

Received 9 May 1960

IN order to obtain specific heats from the data of sound velocity in liquefied gases under high pressure, we have to make use of the compressibility coefficient of the liquid. However, except for helium and hydrogen, data of this kind are rather rare. Because of this, we have started an investigation on the density variation of liquefied gases such as oxygen, nitrogen, argon, neon, etc., as a function of temperature up to 150 kg/cm². So far measurements on liquid oxygen between 90° K and 65° K have been carried out. To a first approximation, a straight line is found for $\rho = f(P)$. From these measurements we have calculated the variation as a function of temperature of the isothermal $(\partial\rho/\partial P)_T$.

Experimental method and apparatus

The apparatus is roughly the same as that which we used for our preliminary measurements. It is shown in Figure 1.

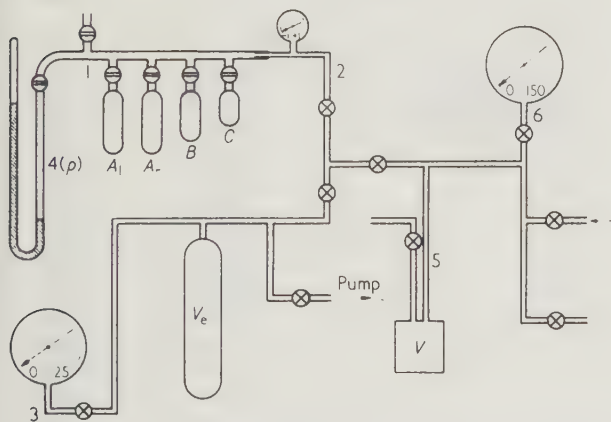


Figure 1. Apparatus for the measurement of density as a function of pressure

We used several calibrated volumes:

V , the condensation volume. At 273° K and 1 kg/cm², V is 97.17 cm³.

V_e , the metal expansion volume. About 4 l.

A_1 , A_r , B , C , four glass expansion volumes of different sizes.

Each of these volumes is thermostatted to within 0.01° K.

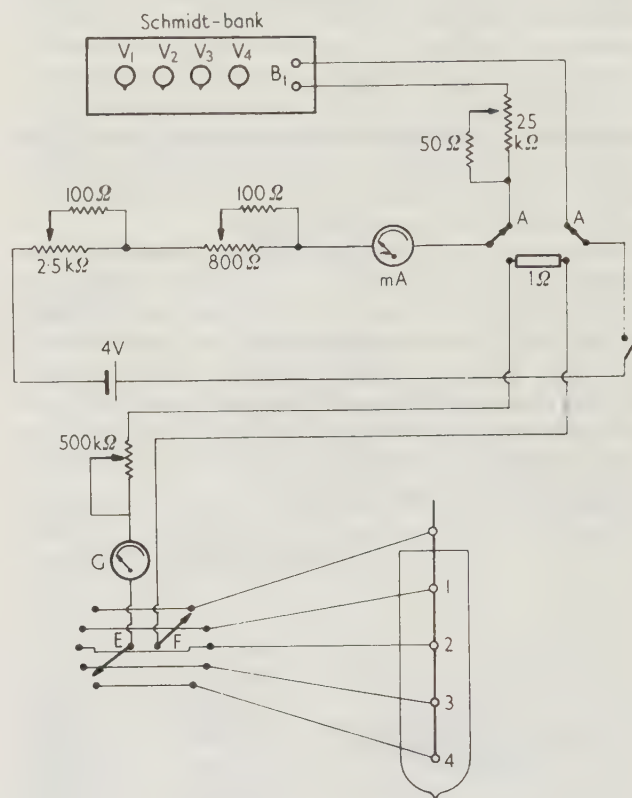


Figure 2. Electrical circuit of the apparatus

The volume V has been calibrated separately with mercury and with distilled water. The dependence of this volume on temperature and pressure is calculated with the help of experimental data¹ and of the theory of elasticity.² The pure gas is condensed in this carefully calibrated volume V at the boiling temperature. In order to determine the mass of the liquid contained in this volume, the vessel is warmed up to room temperature and the gas expands into V_e . With the aid of the P, ρ, T relations at room temperature, it is possible to calculate this mass.

Several corrections have to be made, e.g. gas and liquid correction in the capillary tubes. The liquid present in the capillary tubes leading to the condensation vessel adds to the liquid volume, and this correction is important even at low pressure. The temperature of the top of this liquid level in the capillary tube is determined from the pressure.

Thus an exact knowledge of the temperature gradient along the tube is necessary to estimate the height of this liquid level. For this purpose we used a set of four thermocouples placed along the tube (Figure 2). The density is then given by

$$\rho = \frac{M - M_g - M_l}{V(PT)}$$

where M_g and M_l are the gas and liquid corrections, respectively.

To measure the variation of the density as a function of pressure and especially $(\partial\rho/\partial P)_T$, we have preferred another procedure. Starting with the liquid under high pressure, the pressure is successively lowered by expanding a quantity of gas into the glass expansion volumes. A determination of this amount allows calculation of the loss of mass and the density variation for each step. When vapour tension is reached, a direct measurement with V gives the absolute value of the density.

The temperature is measured with a platinum resistance thermometer calibrated with a standard thermometer provided by Dr. H. Van Dijk of Leiden, and calibrated by him. High pressure measurements are carried out with two Heise Bourdon manometers. The oxygen (purity of the gas is between 98.9 and 99.2 per cent) used is delivered in high pressure cylinders by the firm of Sogaz at Haren near Brussels. This gas is condensed twice, so the purity in the liquid phase is near 99.95 per cent.

Table 1. Experimental Results

T (°K)	P (kg/cm ²)	ρ (g/cm ³)
64.66 (Resistance thermometer 0.760062 Ω)	148.17	1.2778
	136.77	1.2758
	125.90	1.2743
	115.32	1.2728
	104.76	1.2701
	83.35	1.2685
	72.57	1.2671
	61.80	1.2657
	50.90	1.2642
	40.12	1.2633
	29.04	1.2621
	7.96	1.2608
	7.82	1.2591
74.77 (Resistance thermometer 0.99062 Ω)	148.92	1.2345
	138.00	1.2333
	128.00	1.2316
	117.85	1.2300
	107.57	1.2284
	97.29	1.2267
	86.90	1.2249
	76.27	1.2232
	66.72	1.2209
	55.27	1.2197
	44.75	1.2180
	34.20	1.2168

Table 1—continued

T (°K)	P (kg/cm ²)	ρ (g/cm ³)
80.18 (Resistance thermometer 1.11546 Ω)	148.17	1.2138
	138.02	1.2120
	128.23	1.2100
	118.12	1.2083
	107.85	1.2063
	97.77	1.2046
	87.53	1.2028
	77.49	1.2011
	67.62	1.1993
	57.53	1.1976
	47.42	1.1958
	16.35	1.1899
	6.60	1.1883
85.41 (Resistance thermometer 1.23725 Ω)	149.10	1.1923
	139.07	1.1900
	128.34	1.1879
	117.80	1.1858
	107.10	1.1836
	96.65	1.1817
	86.07	1.1794
	75.46	1.1775
	64.75	1.1755
	54.20	1.1734
	43.88	1.1717
	33.20	1.1697
	22.44	1.1680
	12.50	1.1662
90.29 (Resistance thermometer 1.35252 Ω)	146.51	1.1707
	139.95	1.1665
	125.78	1.1664
	115.87	1.1643
	106.08	1.1628
	96.10	1.1602
	86.45	1.1582
	76.55	1.1561
	66.93	1.1540
	57.21	1.1520
	47.48	1.1498
	37.70	1.1483
	27.84	1.1462
	18.18	1.1444
	8.57	1.1424
	1.91	1.1413

Discussion and calculation

The pressure domain is too small for an exact determination of a variation of $(\partial\rho/\partial P)_T$ with pressure. However, from our experimental data it is possible to calculate an equation of the following form:

$$\rho = A + BP$$

with P in units of kg/cm² and ρ in g/cm³. Thus we obtained:

$T(^{\circ}\text{K})$	$\rho =$
90.29	$1.1408 + 1.991 \times 10^{-4} \times P$
85.41	$1.1634 + 1.904 \times 10^{-4} \times P$
80.18	$1.1872 + 1.787 \times 10^{-4} \times P$
74.77	$1.2111 + 1.589 \times 10^{-4} \times P$
64.66	$1.2581 + 1.281 \times 10^{-4} \times P$

We have also calculated, starting from these equations, the variation of A and B as a function of temperature

$$A = 1.5656 - 4.896 \times 10^{-3} T + 2.136 \times 10^{-6} T^2$$

$$B = (-0.53327 + 0.02824 T) 10^{-4}$$

From our experimental data the following thermodynamic properties were calculated:

W : the velocity of sound;

C_V, C_P : the specific heats;

γ : Poisson's ratio.

This is done with the help of three well-known equations:

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -\frac{2T}{\rho^3} \left(\frac{\partial \rho}{\partial T}\right)^2 + \frac{T}{\rho^2} \left(\frac{\partial^2 \rho}{\partial T^2}\right) \quad \dots(1)$$

This gives $C_P(P)$ and we used known values of the vapour pressure curve² as integration constants. Further, we have

$$W^2 = \frac{\gamma}{\left(\frac{\partial \rho}{\partial P}\right)_T} \quad \dots(2)$$

and, finally,

$$\gamma = 1: \left(1 - \frac{\left[\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P \right]^2 \times T}{\left(\frac{\partial \rho}{\partial P} \right)_T \times C_P} \right) \quad \dots(3)$$

The results which were obtained are given in Table 2. Tables 3, 4, and 5 give the comparisons of our measurements and other known results.

Table 2

T ($^{\circ}\text{K}$)	P (kg/cm^2)	$(\partial \rho / \partial P)_T \times 10^{10}$ ($\text{g}/\text{cm dyn}$)	C_P ($\text{cal}/\text{g. deg. K}$) (see ref. 3)	W (m/sec)	γ
65	0	1.328	0.397	1,118	1.66
	50		0.396		
	100		0.394		
	150		0.393		
70	0	1.472	0.399	1,060	1.66
	50		0.397		
	100		0.394		
	150		0.393		
80	0	1.760	0.402	971	1.66
	50		0.400		
	100		0.398		
	150		0.396		
90	0	2.048	0.406	904	1.67
	50		0.403		
	100		0.400		
	150		0.398		

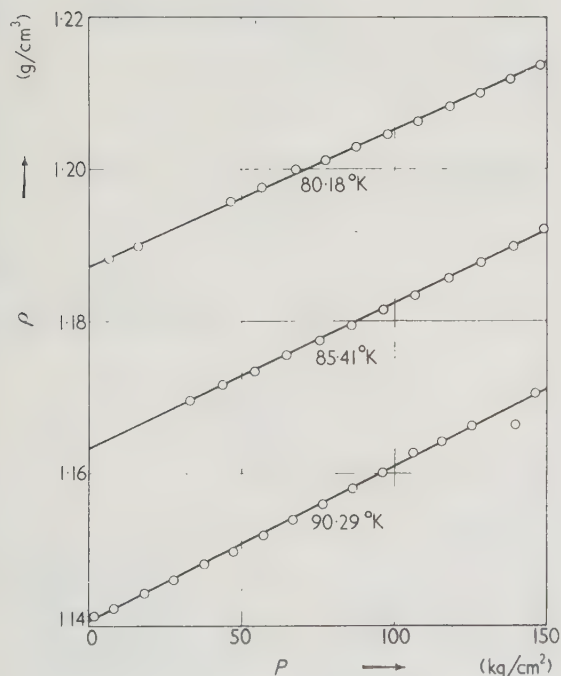
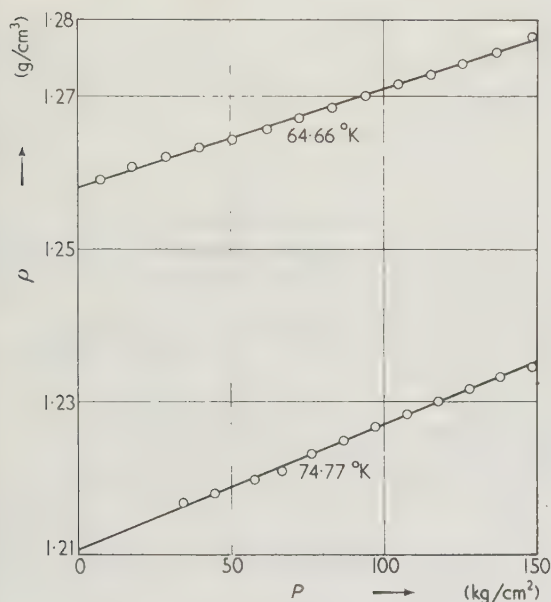


Figure 3. Experimental results: density of liquid oxygen as a function of pressure

Table 3. Comparison of Results for Density at the Vapour Tension

T (°K)	ρ (g/cm ³)	ρ (g/cm ³)	References
	Louvain measurements	Existing measurements	
92.00	1.1335	1.1240	4
89.00	1.1470	1.1479	5
90.65	1.1395	1.1181	6
90.18	1.1417	1.1447	7
91.00	1.1380	1.1415	8
89.55	1.1445	1.1320	9
78.15	1.1961	1.1953	10

Table 4. Comparison of Results for the Velocity of Sound

T (°K)	P (mm Hg)	W (m/sec) exp. (reference 11)	W (m/sec) calc.
90.30	771	902.91	902
77.40	157	1,007.27	992*

* This large deviation is caused by the fact that C_p is not well known.

We take this opportunity of expressing our thanks to the Belgian Ministry of Education for their financial help during this investigation, which was carried out within the framework of the National Research Centre. We also thank the Belgian Institute, the I.W.O.N.L. (Instituut tot Aanmoediging van het wetenschappelijk onderzoek in nijverheid en landbouw), from which one of us obtained a fellowship.

Table 5. Comparison of Results for Expansion Coefficient

T (°K)	$\frac{1}{V} \left(\frac{\partial V}{\partial T} \right) \times 10^3$ Our measurements	$\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)$ Other authors	Reference
90.31	3.95	4.00×10^{-3}	12
		4.12×10^{-3}	5
77.35	3.81	3.85×10^{-3}	5
90.00	3.95	—	
80.00	3.84	—	
70.00	3.73	—	
65.00	3.68	—	

REFERENCES

1. BEENAKKER, J. J. M., and SWENSON, C. A. 'Total Thermal Contractions of some Technical Metals to 4.2°K.' *Rev. sci. Instrum.* **26**, 1204 (1955)
2. PRESCOTT, J. *Applied Elasticity* (Dover, New York, 1946)
3. GIAUQUE, W. F., and JOHNSON, H. L. *J. Amer. chem. Soc.* **51**, 2300 (1929)
4. LIVEING and DEWAR, J. *Phil. Mag.* **40**, 268 (1895)
5. BALY and DONNAN, J. *chem. Soc.* **81**, 911 (1909)
6. DEWAR, J. *Proc. roy. Soc. A* **73**, 251 (1904)
7. PORTER. *Commun. phys. Lab. Univ. Leiden* **117** (1911)
8. MATHIAS and KAMERLINGH ONNES. *J. Amer. chem. Soc.* **51**, 2300 (1929)
9. *Smithsonian Tables* (Smithsonian Institute, Washington, 1956)
10. BILTZ, FISCHER, and WUNNENBURG. *Z. anorg. Chem.* **193**, 358 (1930)
11. VAN ITTERBEEK, A., and VAN DAEL, W. 'Measurements on the Velocity of Sound in Liquid Oxygen, Nitrogen and Mixtures of Nitrogen and Oxygen under Pressure.' *Meeting 1st Comm. Intern. Inst. Refrig., Delft* (1958)
12. KITTEL. *J. Chem. Phys.* **14**, 614 (1946)

A Low Temperature Plant for the Production of Heavy Water

J. Hännny Sulzer Bros. Ltd, Winterthur, Switzerland

Received 4 August 1960

HEAVY water is the oxide of deuterium, a hydrogen isotope whose nucleus contains a neutron in addition to the normal proton, so that its atomic weight is not 1, as with hydrogen proper, but 2. Water in which normal hydrogen atoms are replaced by deuterium atoms is about 10 per cent heavier than ordinary water. In appearance and in chemical behaviour this heavy water can hardly be distinguished from H_2O , but it nevertheless has certain special virtues and in particular is an excellent moderator for nuclear reactors.

The purpose of a moderator is to slow down by elastic impacts the speed of the fast neutrons produced by the fission of a nucleus of uranium-235. Since slower neutrons are more easily captured by other uranium nuclei, the moderator contributes to the initiation and maintenance of a chain reaction. It is important, however, that the moderator should only slow down the neutrons, and should actually capture as few as possible. Heavy water captures only one neutron for every five hundred absorbed by ordinary water, and the critical quantity of natural uranium—the quantity needed to initiate a chain reaction—is only 5 tons with a heavy water moderator as compared with 50 tons with a moderator consisting entirely of graphite.

If the fuel elements used are enriched with the fissile uranium-235, natural water can be employed as a moderator. Even in reactors of this type, however, the use of heavy water is still preferable, since it economizes the neutrons on which the chain reaction depends, and neutron economy is equivalent to better utilization of the available fuel.

The principal properties of heavy and natural water are compared in Table 1.

Table 1. Physical Properties of Heavy and Natural Water

	D_2O	H_2O
Molecular weight	20.03	18.016
Specific gravity	1.107	1.0
Boiling point (°C)	101.4	100.0
Freezing point (°C)	+3.81	0.0
Maximum density at (°C)	11.2	3.98
Critical temperature (°C)	371.5	374.2
Heat of evaporation (kcal/kg)	495.2	533.3

Principle of heavy water production

The production of heavy water is complicated by a number of difficulties. Heavy water is present in ordinary water, but only in a proportion of 1 part in 7,000. This low concentration means that very efficient methods of separation must be used to obtain heavy water of 99.8 per cent purity, which is the figure required for nuclear reactors.

All the production methods in practical use are based on an exchange process. It is immaterial whether the enrichment proceeds directly, i.e. in heavy water itself, or in some other deuterium compound.

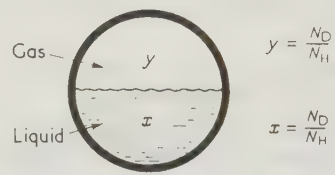
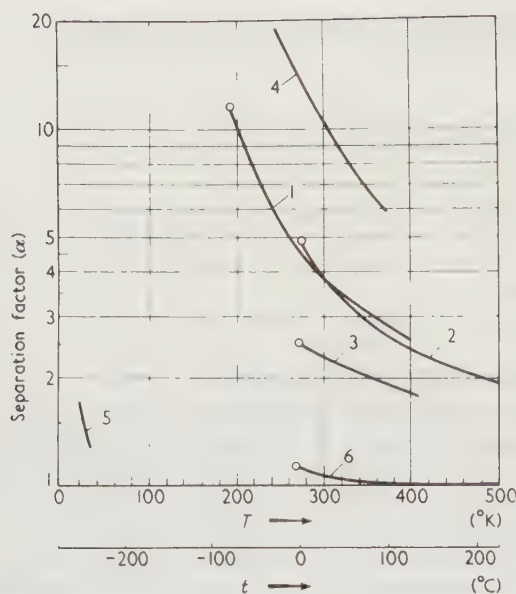


Figure 1. Separation factor of deuterium exchange

If two phases, for instance a liquid and a gas, are brought into intimate contact in a container (Figure 1), as they may be, for example, by vigorous shaking, and if each of these phases consists of a mixture of a hydrogen and the same deuterium compound, an exchange or cross-over of some of the deuterium atoms will take place. When equilibrium is restored, there will be more deuterium in the liquid than in the gas. The reason for this—in the case, for example, of liquid hydrogen and deuterium—is that, owing to its higher vapour pressure, the hydrogen vaporizes rather more easily than the deuterium.

It is not essential, however, that the two phases should be the vapour and liquid of the same mixture. There are other partners which are quite suitable for deuterium exchange, as for instance—to name only the most important for technical purposes—water and hydrogen, water and hydrogen sulphide, and ammonia and hydrogen. In most of these cases, however, exchange takes place only in the presence of a catalyst.

If the proportion of deuterium to hydrogen atoms in the liquid is x , and that in the gas y , the exchange process is characterized by the ratio $\alpha = x/y$. Therefore, α is the simple separation factor; it indicates the deuterium enrichment that can be achieved by shaking the mixtures once in a container.



- | | |
|--|---|
| 1. Exchange of $\text{NH}_3\text{-HD}$
(500 atm) | 2. Exchange of $\text{H}_2\text{O-HD}$
(200 atm) |
| 3. Exchange of $\text{H}_2\text{O-HDS}$
(20 atm) | 4. Electrolysis |
| 5. Rectification $\text{H}_2\text{-HD}$
(1.5 atm) | 6. Rectification $\text{H}_2\text{O-D}_2\text{O}$ |

Figure 2. Separation factors of various methods of deuterium production

In the diagram shown in Figure 2 the separation factor is plotted as a function of temperature for a number of exchange processes. The considerable differences in α for the various pairs of mixtures is apparent and the marked influence of temperature will also be noted. While separation factors of 10 are attainable with electrolysis, the factor for simple water rectification is only 1.05.

At first glance, it would naturally seem preferable to choose the method offering the highest separation factor. The economy of the process, however, is affected by a number of other considerations. Thus the power requirements for dissociation of water by exclusively electrolytic methods are relatively high. Clusius indicated, as early as 1949, a specific power input of 120–150 kW.hr/g of heavy water, whereas the plant at Ems which will be described below requires only about 2–3 kW.hr/g.

Other methods have to be carried out either at very high pressures or at very low temperatures, or else extremely toxic, corrosive, or explosive gases have to be handled—all factors which affect the technical practicability of the methods. Optimum conditions may be attained by the concerted use of several methods; but their attainment also depends on whether a heavy water plant can be combined with other manufacturing processes making use, for instance, of hydrogen. At Ems three methods are employed in conjunction: electrolysis, rectification of hydrogen and deuterium, and rectification of natural and heavy water.

The extraction of 99.8 per cent heavy water from natural water with an initial concentration of only 1/7,000

requires an overall separation factor of 3,500,000. The figures of 1.05 or 10 attainable in a single step are puny by comparison, and must be multiplied many times to enable the desired goal to be reached. This is done in rectification columns.

The liquid phase is fed to the top of a column filled with packings (Figure 3). An equal number of hydrogen atoms in the gaseous phase must now rise in counterflow from the bottom of the column. Owing to the large contact surfaces created by the packings the equilibrium condition defined by the separation factor α is established at every point of the column, i.e. at any cross-section the deuterium concentration is y in the gas and x in the liquid, x exceeding y by the margin of the separation factor. The liquid stream thus contains more deuterium atoms than the gas stream, and deuterium is therefore carried downwards. Whether enrichment takes place or not depends only on what happens to the two streams at the bottom of the column. In the rectification process the liquid that trickles down is quite simply re-evaporated in a vessel known as a still-pot or reboiler. For a time, therefore, no product is drawn off. Also, since the deuterium is carried downwards without anything being removed, it must obviously accumulate at the bottom of the column.

On the right-hand side of Figure 3 the concentration is plotted against the height of the column. The diagram indicates how the concentration gradually begins to rise from the bottom end upwards until the equilibrium state

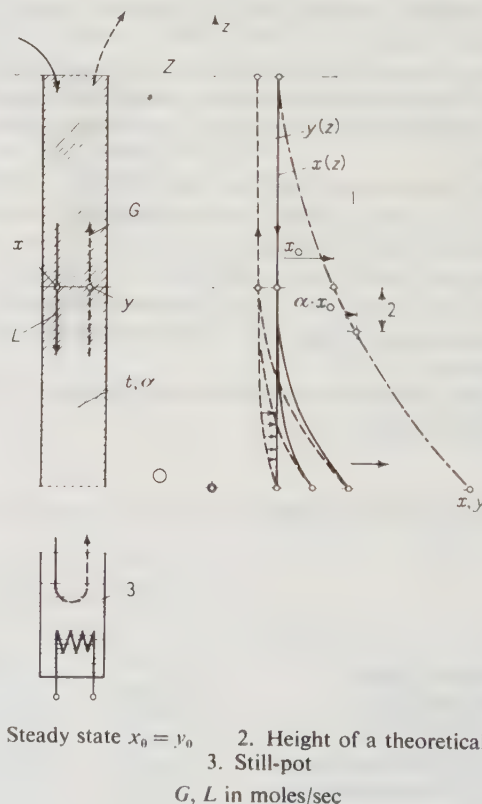


Figure 3. Method of operation of an exchange column

represented by the chain-dotted line is reached. The concentrated product can now be withdrawn at the bottom. It is most important, however, that no more product is withdrawn than is actually being carried down the column. If this should happen, the concentration would fall; in fact, the concentration at the bottom of the column can be controlled by the amount withdrawn.

These are the essential facts about heavy water production. The rest depends only on accessories, that is to say on the equipment required for carrying out the exchange process. Surprisingly enough, the rectifying columns proper form only a very small part of the whole installation.

Figure 4 shows the three production phases of the plant at Ems. The electrolyzers of the ammonia synthesis plant are connected in cascade for heavy water production. Somewhat more water is fed to each stage than is dissociated into the components oxygen and hydrogen by the electric current. The excess water is condensed out of the gases produced and is supplied to the next stage as feed water. In this way approximately seven-fold preliminary enrichment is attained. The preconcentrate, containing about 0.1 per cent D_2O , is split up in its entirety into oxygen and hydrogen in the last electrolyser. The hydrogen, of which about 400 standard cubic metres is produced

per hour, is stored in an intermediate gas-holder and is later cooled to about $-250^\circ C$ in the low temperature plant. After liquefaction at this temperature, it is conducted to the low temperature rectifying column. At these low concentrations the deuterium atoms occur only in combination with hydrogen atoms in the form of hydrogen deuteride (HD). Since the equilibrium between H_2 , HD, and D_2 is 'frozen' at this low temperature, the best possible product of rectification is 100 per cent hydrogen deuteride, which would correspond to 50 per cent D_2 . In the plant described here the process is carried only as far as 60 per cent HD, after which the product taken from the column is burnt in a simple oxyhydrogen burner. The resulting 30 per cent heavy water preconcentrate is then led to a final rectifying column which rectifies water and heavy water under vacuum at about $60^\circ C$ and yields the desired product of 99.8 per cent purity.

This combined process offers the advantage that the two rectifying columns can be operated independently of each other. The final column can also be used for regenerating any highly concentrated heavy water waste without undue mixing losses. Another reason for the choice of the combined process was that the simple and reliable method of water rectification was already known and proved, so that the risk involved in the first execution of a plant of this type was greatly reduced.

Method of operation of the low temperature plant

Figure 5 shows the low temperature installation proper for the rectification of the liquid hydrogen at $-251^\circ C$

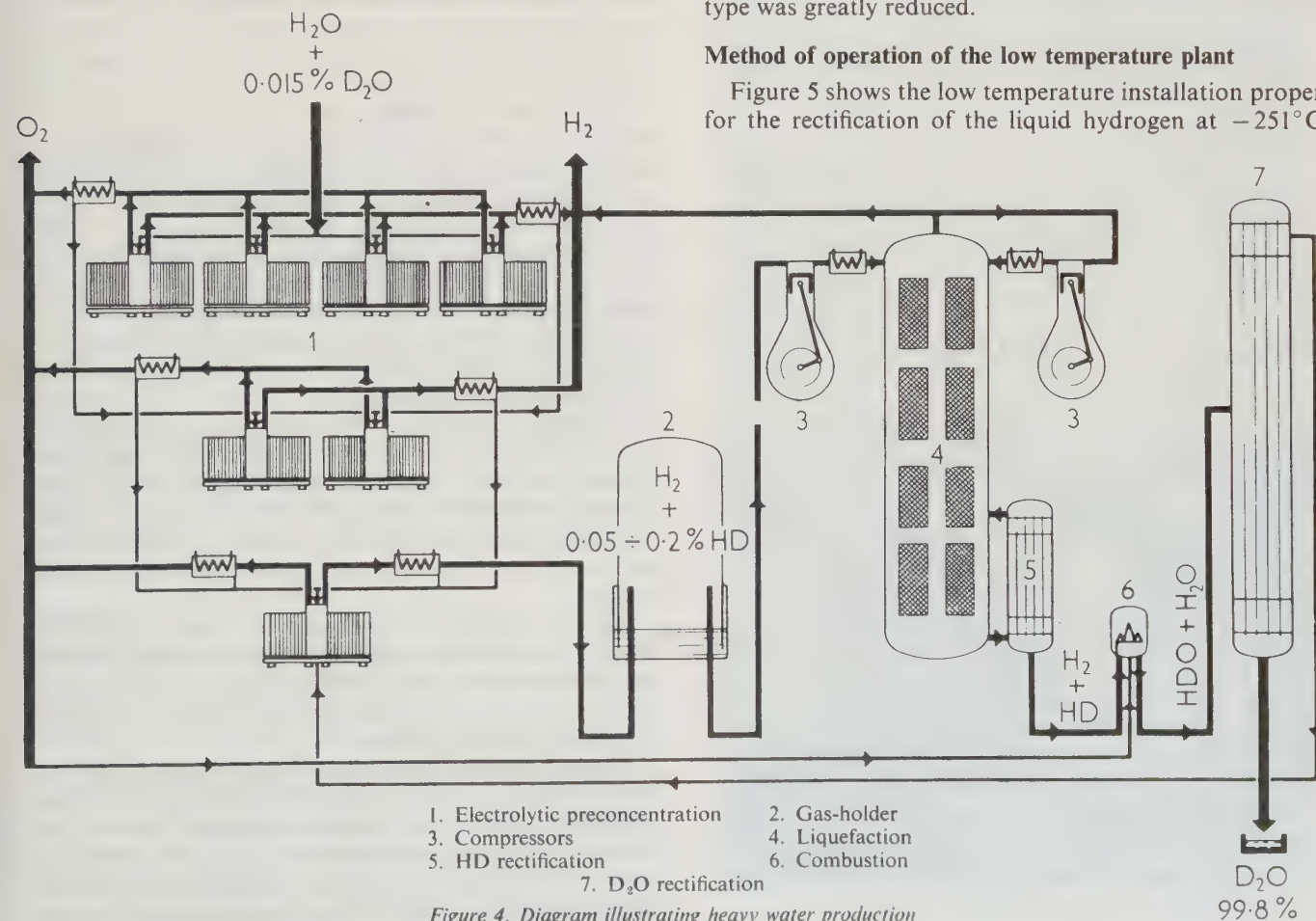


Figure 4. Diagram illustrating heavy water production

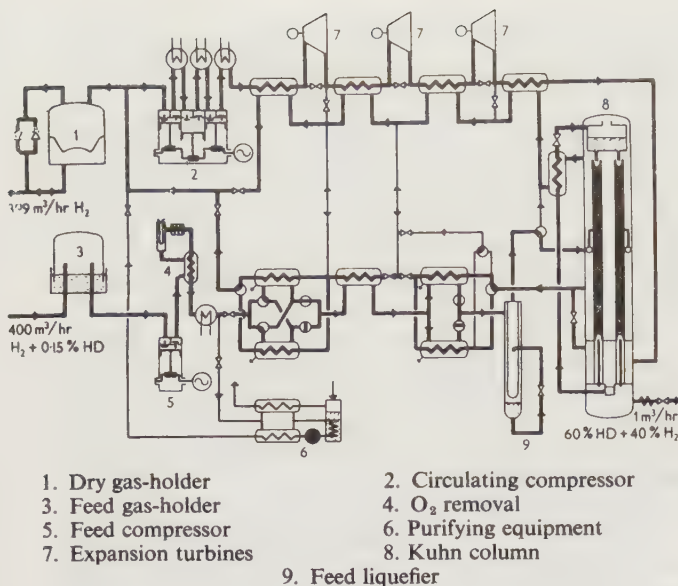


Figure 5. Diagram of the H_2 -HD rectifying plant

(22°K). On the extreme right of the illustration is the rectifying column of the Kuhn type. It consists of a series of tubes connected in parallel in which the rectification process takes place. Refrigerating machinery is needed for operating the column. It supplies the refrigeration required for cooling the column and for liquefying the hydrogen and consists of a compressor, heat exchangers, and expansion turbines.

A three-stage oil-free piston-type compressor brings the hydrogen gas up to a pressure of about 14 atm (abs). It is then cooled down to liquefaction point by the returning gas in a series of heat exchangers, each followed by an expansion turbine in which it gives up energy to the turbine shaft. The last heat exchanger takes the form of an ordinary Joule-Thomson exchanger, as used in plants for the liquefaction of air. The hydrogen, which is already somewhat moist, is now introduced into the bottom part of the column to heat the still-pots of the individual rectifying tubes and is liquefied while giving up heat to these tubes. The liquid is collected and sub-cooled in a further heat exchanger before being expanded and introduced into a container at the top of the column. From here the liquid hydrogen trickles down, evenly distributed by capillaries among the various rectifying tubes, and absorbs deuterium in contact with the rising vapour. Reaching the bottom of the tubes, it is again evaporated by the condensing hydrogen on the outside. It then flows back through the tubes in countercurrent to the liquid, is withdrawn at the head of the column, and returned through all the heat exchangers previously mentioned to the suction side of the compressor. Consequently, it first sub-cools the liquefied hydrogen and later gives up its refrigeration to the fresh incoming hydrogen, absorbing heat in the process, until it is once more at room temperature. This completes the refrigeration cycle proper.

It will be noted that hardly any refrigeration is given up to the outside, with the exception of plant losses. The same amount of hydrogen as is liquefied in the heating jacket at the bottom of the column evaporates at the same time in the inside of the tubes. Although over 1,000 l. of liquid hydrogen are produced in the plant every hour, a comparatively small refrigeration capacity is sufficient.

The product, now rich in deuterium, is withdrawn through capillaries at the bottom of the tubes. A corresponding amount of deuterium must be constantly supplied to the various tubes halfway up the column. This is the pre-enriched feed hydrogen coming from the electrolysis plant. As yet, however, it contains many impurities and therefore has not only to be cooled but also to undergo a purifying process before it enters the column. It is first compressed to about 3.7 atm (abs) in a feed compressor, after which oxygen is extracted from it in a catalytic contact furnace. This oxygen then combines with hydrogen to form water. The feed hydrogen afterwards goes to two interchangeable heat exchangers in which it is cooled by returning gas to about -100°C , so that practically all the water is frozen out of it. Only one of these exchangers is in operation at any time, while the second is being thawed by the fresh incoming gas. After having been cooled to about -200°C in a further exchanger, the feed flows to another interchangeable pair of exchangers, as the saturation temperature of nitrogen has now been reached. Electrolysed hydrogen may contain up to two parts of nitrogen per thousand, and this is now frozen out in one of the last two exchangers. When a sufficient amount of nitrogen has been collected, the second exchanger comes into operation, while the first is thawed out and the nitrogen led away in the liquid state. In the last stage of purification the whole feed flow is liquefied and re-evaporated. The feed liquefier consists, essentially, of a simple tube on the outside of which the hydrogen condenses. The liquid is then expanded and introduced into the inside of the tube, where it again evaporates, leaving the last impurities behind. The feed liquefier prevents any obstruction of the feed capillaries and the column.

The overall balance of the process shows that about 400 m³ of hydrogen are introduced through the feed compressor per hour, of which 1 m³/hr is withdrawn at the bottom of the column, while 399 m³ flow back through the feed exchanger to join the hydrogen used for refrigeration and to take part subsequently in the ammonia synthesis process.

The process extracts a small amount of deuterium from a flow of hydrogen serving another manufacturing purpose and therefore takes 'parasitic' advantage of the electrolytic enrichment, the costs of which are debited to the ammonia synthesis process.

At the bottom of the diagram, purifying equipment is shown; this is required for the first commissioning of the installation. It is of the greatest importance that the gas flowing in the refrigerating circuit should be absolutely pure, as otherwise the expansion turbines might become choked with ice. When the installation receives its first

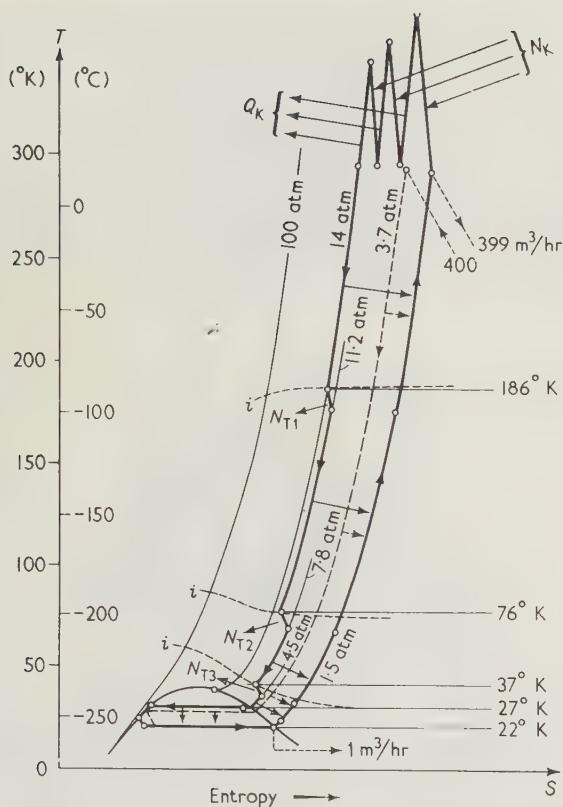


Figure 6. Temperature-entropy diagram of the refrigerating process

charge, the hydrogen is therefore cooled with liquid air and cleaned in an activated carbon filter. A dry gas-holder stores up this pure charge when the plant is out of operation.

The refrigeration cycle illustrated in Figure 5 is plotted in the temperature-entropy diagram in Figure 6. The first expansion of the gas after three-stage compression takes place in two turbines connected in series, so that in all there are four turbines, two of which operate below the temperature of liquid air and one only about 30°C above absolute zero. The installation differs from known gas liquefying or separating systems in that all the turbines are connected in series, so that the total amount of gas handled by the circulating compressor flows through each of them.

We will next discuss the component parts of the heavy water separation plant.

Compressors

Both compressors operate without any oil contamination.¹ The piston rod is guided at two points outside the cylinder, in which the piston moves freely, sealing being obtained by labyrinth grooves. The stuffing-box is also provided with labyrinth rings, so that the gas handled cannot come into contact with oil at any point. As no stuffing-box losses are admissible, the whole crankcase of the compressors at Ems is made gas-tight and is connected to the gas-holder by way of an oil trap. In practice this trap has hardly any work to do, since the pressure in the

gas-holder is constant and the gas in the crankcase therefore remains unchanged. An intermediate tapping at the stuffing-box ensures that leakage losses are returned direct to the suction side of the cylinders and do not enter the crankcase at all.

Figure 7 (left) shows the feed compressor. There is a comparatively large valve station (not shown in the Figure) on the suction side of the machine, its size being explained by the fact that it is necessary to aspirate either nitrogen or normal or enriched hydrogen, according to whether the plant is in normal operation or is being flushed with nitrogen for overhaul purposes.

The circulating compressor of the refrigerating plant (Figure 7 (right)) is a three-stage machine, as already mentioned, and is directly coupled to a 3,000 V driving motor. This compressor also has a completely enclosed crankcase.

The use of oil-free compressors has considerably simplified the design of the low temperature plant, since no equipment is now required for removing oil mist downstream of the compressors and there is no danger of the heat exchangers and the column being fouled.

Vacuum insulation of the heat exchangers

One of the main problems raised by the design of the plant was the layout and insulation of the heat exchangers and control valves. It was not possible to use mineral wool as in ordinary air liquefaction plants, since in two-thirds of the installation the prevailing temperatures are below that of liquid air. However thick the layers of insulation were made, the air contained in them would condense on the inner walls, and there might even be a dangerous build-up of oxygen, involving the risk of explosions if the slightest hydrogen losses should occur. On the other hand it is uneconomical to fill the insulation space with hydrogen, as the thermal conductivity of this gas is about seven times that of air.

To circumvent all these difficulties, vacuum insulation

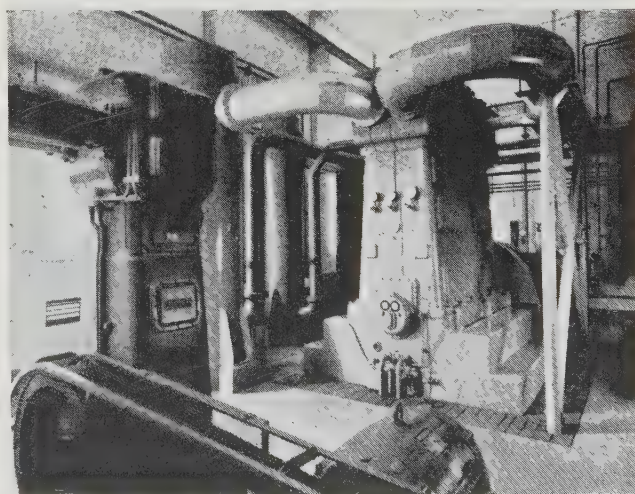


Figure 7. (Left) Feed compressor; (Right) Circulating compressor

was chosen. The designers were aware that it would not be a simple matter to make such large pieces of equipment tight against high vacuum, especially if they contained hydrogen under pressure. A vacuum of at least 10^{-3} torr, or a pressure of about $1/10^6$ atm, is needed for good insulation. On the other hand, the advantages were so attractive that the attempt seemed justified. With high vacuum insulation, when the mean free path of the molecules is longer than the distances between individual units of equipment these distances cease to be important, and the whole plant can be made very compact. In addition, it is not necessary to cool tons of insulating material when the temperatures are being lowered prior to operation, and starting times are therefore much reduced.

A second basic decision affecting the design of the plant was that all regulating valves should be remote controlled with gas under pressure. It has hitherto been the custom in low temperature installations to connect the cold valves to hand-wheels outside the outer jacket by means of spindles of suitable length. This severely restricts the free placing of the control valves, while the numerous spindles cause additional heat and leakage losses. With servo-controlled valves, whose servomotors are also at low temperature, only two small calibre pipes have to be carried to the outside, while the valve can be placed exactly as desired.

Figure 8 shows a cross-section of the vacuum jacket containing the column. There are four such units in the whole plant. The first contains the heat exchangers down to -100°C , the second the exchangers down to -200°C , the third the feed liquefier and final feed heat exchangers, and the fourth the column.

All the vacuum jackets are of the same fundamental design. The heat exchangers and the column are all suspended from long thin stainless-steel rods in a lower space. As stainless steel has a very poor thermal conductivity, undesirable heat gains can be kept to a minimum. The jacket is connected to an oil diffusion pump through a lateral branch. There are no flange connections or other mechanically detachable joints in the jacket itself. All pipes are welded or soldered. All components incorporating flange connections, and particularly the control valves, are mounted under a separate hood in the upper part of the unit. In this upper space a rough vacuum only is maintained, since there is obviously a possibility of hydrogen leaks developing in some of the flanges in the course of time. To ensure good insulation, however, this upper hood is of double-walled design, and the space between the walls is kept under high vacuum as in a Dewar vessel.

The turbines are located laterally on the suction pipe of the diffusion pumps and are also covered by a vacuum hood. Radiation shields of aluminium are fitted inside all the vacuum jackets in order to reduce radiation losses to a minimum. For the purpose of erection and dismantling, the large vacuum jackets can be simply lowered and the hoods over the fittings removed from above. The various units of equipment are then readily accessible from the platforms. The lowering of the vacuum jackets

takes much less time than would the removal, for instance, of slag-wool insulation.

Servo-controlled valves for ultra-low temperatures

Extensive development work made it possible to design servocontrolled changeover and regulating valves which operate reliably even at extremely low temperatures (Figures 9–11). The sectional drawing in Figure 9 shows a three-way valve with low temperature servomotor. The

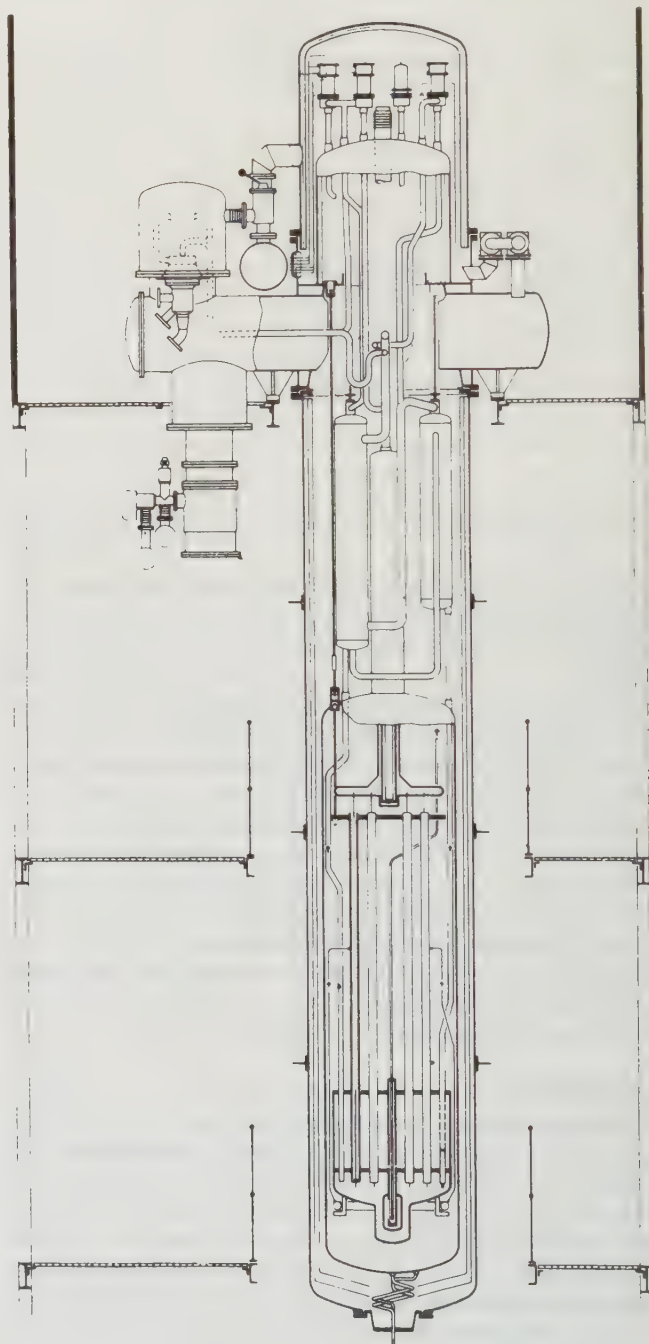


Figure 8. Section through a vacuum jacket with column, heat exchangers, diffusion pump, regulating valves, and expansion turbine

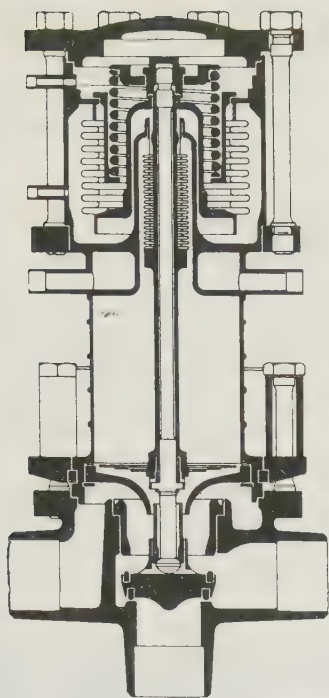


Figure 9. Three-way valve with low temperature servomotor

operative component of the servomotor is a bellows unit that transfers its force through a bell to the central spindle. This in its turn actuates the valve disk. All seals are metallic and are tightened with extensible shank bolts which ensure adequate sealing pressure even when big temperature changes occur. The servomotor spring can be fitted to operate in either direction, so that the valve always takes up the desired position when free of pressure. Hydrogen is of course the only choice for the actuation of the

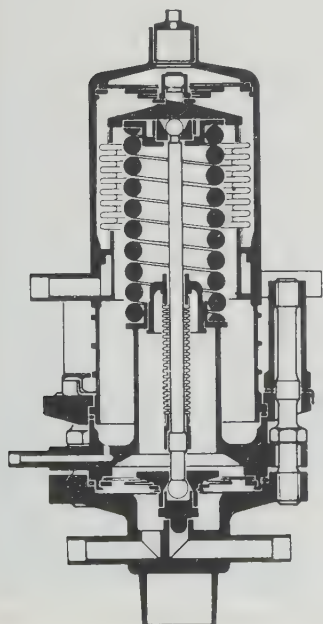


Figure 10. Regulating valve for liquid hydrogen

servomotor, as air would solidify. Even with hydrogen there is some risk of its liquefying when the servomotor operates at a very low temperature level. For this reason the servomotor is separated from the valve by a thin walled stainless-steel cylinder and is warmed by a gas heating system enough to ensure that the control gas cannot condense, although no great losses can occur.

The regulating valves (Figure 10) are similarly designed. The one shown in the Figure is for liquid hydrogen. Whereas in the three-way valve two end positions only are needed, a regulating valve must take up any desired position, and this must be exactly adjustable from outside. To this end the whole valve is made absolutely frictionless. The spindles are held by elastic springs, and the infinitely adjustable control pressure acting on the bellows operates against a spring, so that the pressure directly determines the spring loading and thus the valve position. Here again the servomotor is divided from the valve by a distance piece and separately heated.

Expansion turbines for hydrogen

The most important units in the refrigerating plant are the expansion turbines. Without these no refrigeration

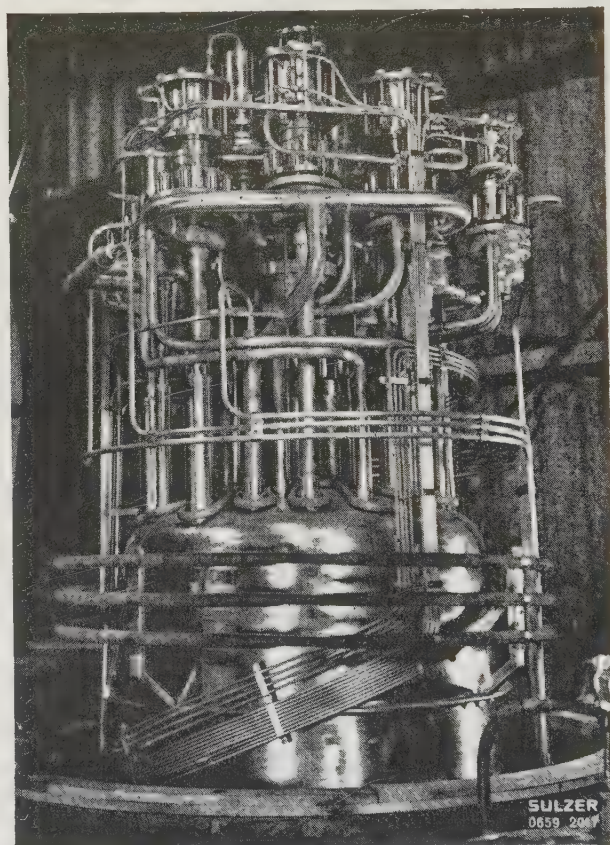


Figure 11. Valve assembly from the side. The cold end of the vacuum jacket carries the valves and is itself supported on the warm tank carrier by means of a thin walled stainless-steel cylinder. The heating coil visible in the Figure is used for heating the whole valve space when overhauls are carried out. The control and heating pipes for all servomotors are also shown

would be produced, and all the other parts of the plant thus depend on their efficient operation.

The installation at Ems is the first hydrogen liquefying plant in which refrigeration is produced exclusively by expansion turbines. Most of the refrigeration required for hydrogen liquefaction is normally obtained from the evaporation of liquid nitrogen, which means that the hydrogen liquefier has to incorporate a complete liquid nitrogen plant.

The turbines (see Figure 12) are, like most expansion turbines for low temperature applications, of the centripetal type, i.e. the gas flows radially inwards through the turbine wheel and leaves in the axial direction. The turbine casing is supported on the warm fixing flange by means of a thin stainless-steel cone, and an internal bearing housing encloses the whole oil-lubricated part of the turbine rotor. The only insulation between the cold turbine casing and the warm bearing housing is provided by high vacuum. The turbine rotor, with a vertical shaft, runs in two oil-lubricated bearings and has an oil brake in the centre to dissipate the excess energy. The turbine wheel is overhung and projects into the cold casing. A magnetic pick-up excited by the bottom end of the shaft measures the turbine speed.

When the turbines are fitted, the gas entering them is first passed through a filter, in order to prevent damage to the inlet and turbine wheels. A hand valve is provided on the inlet and outlet sides to permit the turbines to be removed singly even when the rest of the plant is cold and contains hydrogen.

The design of expansion turbines for hydrogen presents several difficulties. First of all a seal must be provided for a shaft turning at about 100,000 rev/min. The distance between the cold turbine wheel and the warm lubricated bearing is only about 30 mm, yet the temperature difference is over 250°C. It is imperative that no trace of oil whatsoever should be able to find its way into the turbine, and refrigeration losses through the casing and shaft must also be kept low.

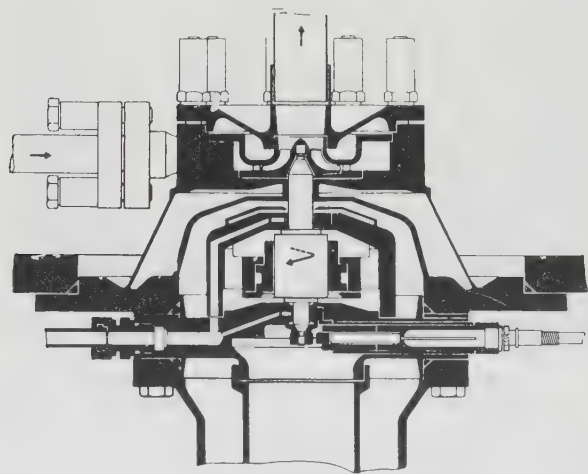


Figure 12. Cross-section through the expansion turbine for hydrogen

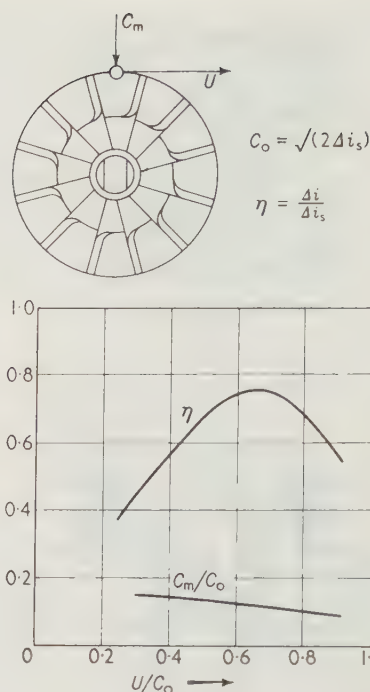


Figure 13. Characteristic of the expansion turbines for hydrogen

A further difficulty arises from the general turbine characteristic (Figure 13). The efficiency reaches its optimum at a figure of about 0.65 for the ratio of the peripheral speed of the turbine wheel U to the head velocity C_0 . This is the velocity attained when the gas is isentropically expanded with the use of the full turbine head. Even at a pressure ratio of about 2, C_0 reaches the speed of sound, which for hydrogen at room temperature is over 1,200 m/sec. The corresponding optimum peripheral speed would thus be 800 m/sec, a figure which cannot be reached with the materials so far available. This means that only a comparatively low head can be attained in one turbine stage, even if peripheral speeds up to 400 m/sec are adopted, and this is one of the reasons why the plant is equipped with four turbines, whereas normal air liquefaction plants have one turbine only.

Hydrogen-hydrogen deuteride rectifying column

Figure 14 shows the low temperature installation with the vacuum jackets lowered. The rectifying column for liquid hydrogen, consisting of 90 parallel tubes, hangs in the foreground. About two-thirds of the length of the column is used for the rectification process proper, while in the bottom third the hydrogen evaporates as it trickles down through the tubes. The hydrogen condenser surrounding the tubes also serves as a liquid container. The feed hydrogen is supplied to the individual tubes through capillaries about half-way up. At the head of the column, thin feed tubes can be seen projecting into each tube of the column. These contain the capillaries for the reflux liquid. The upper liquid tank is hidden under the hood. It has an

extension in the centre to take the level measuring equipment. Reflux in the column is kept constant by exact control of the liquid level in this tank. The last heat exchangers for partial condensation of the circulating gas are also visible above the column.

Vacuum plant

The vacuum plant (Figure 15) embraces three different systems. The system generating the high vacuum in the main vacuum jackets comprises a mechanical rough vacuum pump and a Roots blower, both connected to a header to which the four oil diffusion pumps are joined up in parallel. The high vacuum is therefore generated in three stages. A second system again includes a mechanical rough vacuum pump with a single diffusion pump connected to it and operating on a high vacuum header. The spaces between the double walls of the valve hoods and the hoods over the turbines are connected to this header. A third system with a single rough vacuum pump evacuates the inside of the valve hoods, where a less stringent

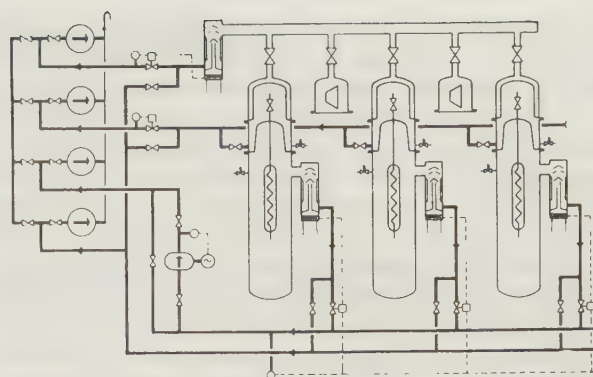


Figure 15. Diagram of the vacuum plant

vacuum is required. The three normal pumps are supplemented by a stand-by which can take over for any of the other units through a header, and can also pump out any vacuum jacket that has been shut down by way of a separate pipe before it is connected up to the main header again. Each of the systems has its own vacuum monitor which isolates all the jackets by pneumatic means as soon as the pressure rises above a certain value. At the same time all the electrical equipment, such as the heating system of the diffusion pumps and the electric vacuum measuring units, is switched off to prevent any oxyhydrogen gas present in the vacuum space from being ignited by the electric current.

Control room

The whole heavy water plant is supervised from a central control room. A diagram of the plant, as shown in Figure 5, appears on one of the walls. Hand-wheels are fitted to correspond with the positions of the valves in the diagram, which greatly simplifies control of the plant. Automatic recording apparatus for temperatures, pressures, liquid levels, and vacua can be seen in the background, and on the left the revolution indicators for the turbines.

Hydrogen deuteride combustion

The combustion equipment takes up less than 1 m² of floor area. It comprises a burner followed by a flame tube of high temperature steel, a cooler, several changeover valves, and a cold trap for freezing the heavy water out of the outgoing excess oxygen. Here again a safety system ensures that no oxyhydrogen explosions can occur.

Heavy water rectification

Figure 16 shows the heavy water rectification column. The liquid flowing down from the burner is collected in a container and fed by way of a float regulator to the feed evaporator. The feed is metered by setting the desired heating performance, and the feed vapour is then distributed through capillaries to the individual rectifying tubes. Here, heating of the still can be done with ordinary steam, and the reflux is produced at the head of the column in a simple water-cooled condenser. From here it goes to a

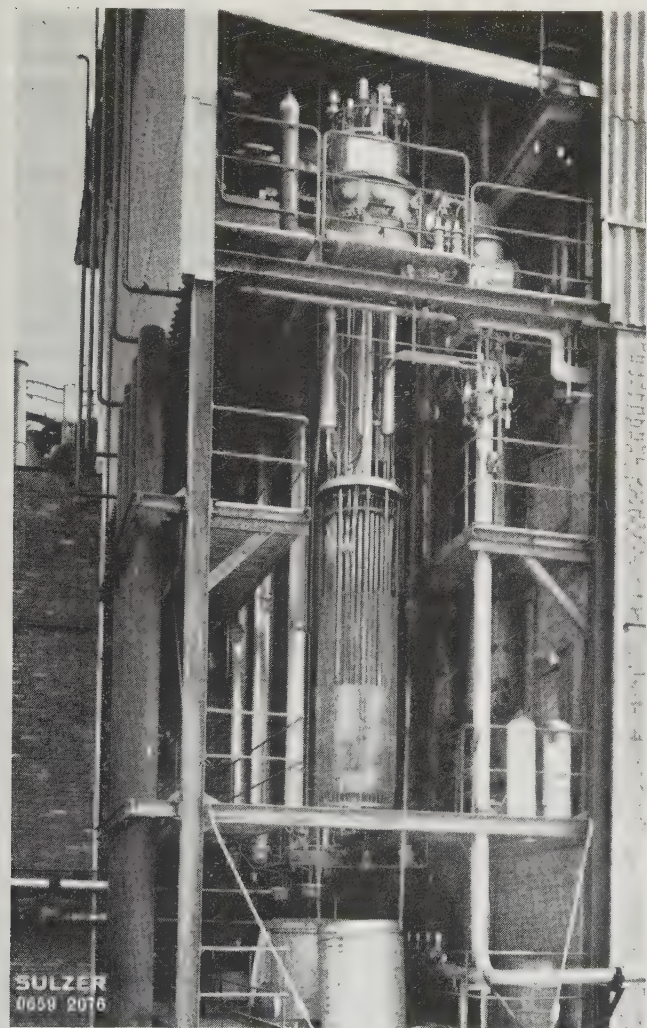


Figure 14. Rectifying column for liquid hydrogen

vessel whose overflow level determines the reflux quantity. The overflow of this vessel is the head product. It is collected in a separate receiver and returned to the electrolyzers. The heavy water is withdrawn in the form of steam through capillaries at the bottom of the tubes. Removal is automatically controlled by a concentration regulator. This employs a simple glass float which is calibrated to the specific gravity of heavy water and is scanned by photocells. When the concentration begins to fall, the float moves downwards, causing a reduction in the amount of product withdrawn. About 1 l./hr of 30 per cent heavy water in all is introduced into the final column per hour, and is there separated into the 'bottom' product of 99.8 per cent

purity and a 'head' product of 3 per cent concentration. The vacuum in the column and in the product condenser is automatically controlled by manostats.

Conclusion

A few comments on the time required for the development of this plant may be of interest. It was necessary first of all to test all the component parts singly, a procedure which was in itself fairly time-consuming.

Wide use was made at this time of the hydrogen liquefier in the Physico-Chemical Institute of Zürich University, which was needed for cooling down the low temperature fittings, testing soldered joints, and calibrating thermocouples. In the same Institute the efficacy of the packings used for separating hydrogen and deuterium was first tested and the feasibility of rectifying hydrogen with Kuhn columns was proved.

Before the final decision was taken to insulate the whole plant with high vacuum, a single vacuum-jacket unit was erected in the open at Oberwinterthur. The same unit, with the same heat exchangers, was later erected practically unchanged in the installation at Ems. Immediately after assembly a vacuum of 10^{-4} torr was attained, so that the decision to carry out the plant with high vacuum insulation at once appeared justified. At Ems it was later possible to generate vacua of up to 10^{-6} torr in the big jackets.

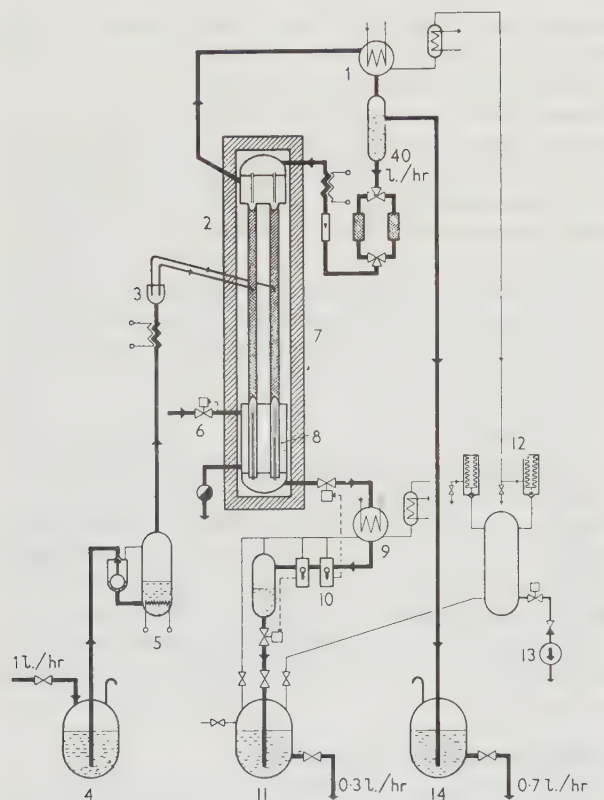
The experimental plant was cooled down to the temperature of liquid nitrogen with a first prototype turbine, so that it was now clear that all the components could be relied upon even at very low temperatures.

It may be mentioned here that the technical realization of the whole plant demanded great personal efforts from all concerned, since hardly a dozen persons were available for the calculation and designing work throughout the development period of just under four years.

We should like in conclusion to express our special thanks to Professor Clusius of Zürich University, to Professor Grassmann of the Swiss Federal Institute of Technology in Zürich, and to Professor Kuhn of Basle University for their valuable assistance, as well as to the Management of the Emser Werke for their close and helpful co-operation.

REFERENCE

1. RITTER, U. 'The Dry-Piston Compressor for Handling Gases and Vapours without Oil Contamination.' *Sulzer Technical Review* No. 2/1958, p. 3



1. Reflux condenser
2. Kuhn column
3. Feed distributor
4. 30% D₂O feed
5. Feed evaporator
6. Vapour
7. Insulation
8. Heating jacket
9. Product condenser
10. Concentration regulator
11. Product (99.8% D₂O)
12. Manostats
13. Vacuum pump
14. Head product (3% D₂O)

Figure 16. Diagram of the heavy water rectification system

The Critical Field of Superconducting Aluminium under Pressure

D. Gross and J. L. Olsen

Institut für kalorische Apparate und Kältetechnik, Eidgenössische Technische Hochschule, Zürich

Received 29 August 1960

THE electronic specific heat of a superconductor in the normal state may be calculated from the observed critical field curve. Similarly, the change in electronic specific heat with pressure may be calculated from the change in critical field under pressure. Such work on a wide range of superconductors¹ has shown that the electronic specific heat is much more sensitive to volume changes than the Sommerfeld free electron theory predicts.

It would obviously be interesting to discover if this volume sensitivity can be understood from a study of the actual electronic structure of a metal. To provide a basis for such an investigation we have thought it useful to collect experimental information on the pressure dependence of the critical field in aluminium. This is the superconductor about whose Fermi surface most is known. The de Haas-van Alphen effect in this metal has been studied extensively by Gunnerson,² and work on cyclotron resonance and on the anomalous skin effect is also available. Detailed theoretical studies have been made by Heine³ and by Harrison.^{4,5}

Grenier⁶ and Muench⁷ have measured the pressure dependence of the transition temperature T_c in aluminium. A calculation of the pressure dependence of the electronic specific heat requires a knowledge of the effect of pressure on the critical field at lower temperatures as well, and we have now made such measurements at temperatures down to around 0.3°K. It is found that the electronic specific heat is highly volume sensitive in this metal too.

In addition to this work on aluminium we have also examined the effect of pressure on the critical field of zinc. Here the technique used for creating the pressure does not yield a pressure which is sufficiently isotropic to allow quantitative conclusions. We include the results here for completeness.

Experimental method

Adiabatic demagnetization of ferric ammonium alum was used to cool the specimens. The salt was mixed with a cold-setting resin ('Prestolith', obtainable from Althaus and Vogt GmbH, Bochum-Harpen) and compressed under a pressure of 500 kgcm⁻² around copper fins. This produced a remarkably stable pill which has now been in use for about 18 months without apparent deterioration. According to Andres⁸ the thermal resistance between

copper and salt is of the order of 2×10^4 deg.cm²W⁻¹ at 0.4°K.

The pressure was made by the ice-bomb technique first used by Lazarev and Kan⁹ in similar experiments on tin and subsequently by several other investigators. The specimens to be put under pressure are enclosed in a thick walled container which is filled with water and which can be firmly closed. On cooling to liquid helium temperature, pressures of about 1,700 atm are developed.

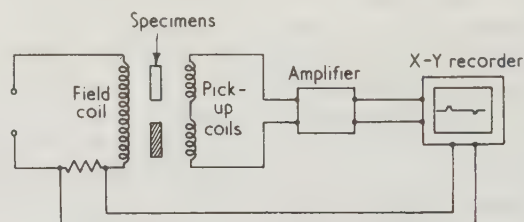


Figure 1. The apparatus

The ice-bomb contained three specimens: one each of aluminium and zinc, and also one of another metal used for pressure calibration. Three other similar specimens were mounted in a similar container without ice, and both containers were connected thermally to the copper vanes in the salt pill. Both containers were therefore at the temperature of the salt. The temperature adjustment in the pressure container was excellent; in the container without ice it could only be maintained by soldering the specimens to the container.

The critical fields were measured in the following manner. A magnetic field which increased linearly with time was applied, and the difference in the rate of change of flux in two coils wound round the containers was observed. This was done by amplifying and recording the output from the coils which were wound in opposition. Figure 1 shows a schematic diagram of the apparatus, and Figure 2 shows typical recordings. When nothing happens, the output voltage is zero, but deflections occur when one or the other of the specimens becomes normal. The rates of increase of field could be varied between 0.1 and 0.5 gauss sec⁻¹. Too rapid an increase led to smeared-out transitions, and usually a rate of change of 0.15 gauss sec⁻¹ was used.

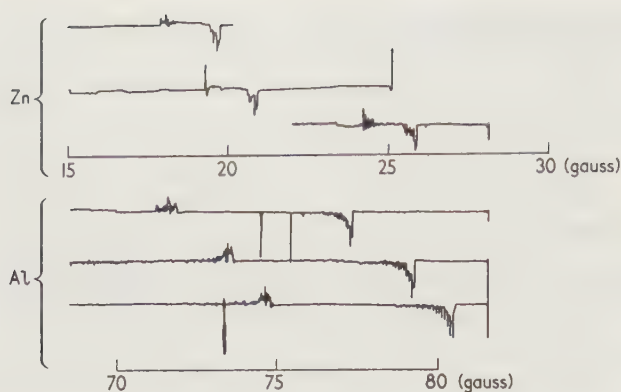


Figure 2. Typical recorder traces; the downward deflections come from the specimen at zero pressure

The first measurements were made using elliptic specimens 3 mm in diameter and 30 mm long, but it was found that the transitions were too wide to be properly interpreted. The measurements shown here were therefore made with specimens in the form of wires 1 mm in diameter and 30 mm long. The very small indium joints used to make thermal contact between specimens and container caused a local distortion of the magnetic field. This was too limited in extent to affect the results.

The pressures were measured in each run by means of a specimen with known $\partial H_c/\partial p$ (H_c is the critical magnetic field, and p is the pressure). Alekseevskii and Gaidukov¹⁰ have made measurements on cadmium, and we used this substance as a pressure calibrator in our first experiments. Unfortunately, it now appears that the pressure effect in cadmium is sometimes sufficiently anisotropic to give highly misleading results for the pressure in the ice-bomb. This led to an overestimate of $\partial H_c/\partial p$ at low temperatures in preliminary measurements on aluminium reported briefly elsewhere.¹¹ In the work reported here we used indium to measure the pressure. Indium is also anisotropic, but this metal appeared to give consistent values of the ice-bomb pressure. This is presumably because indium flows so easily under pressure that anisotropic stresses cannot build up. Muench⁷ also confirms the reliability of indium for ice-bomb calibration.

Results

The critical field $H_c(p)$ at pressure p is given approximately by

$$H_c(p) = H_0(p) \{1 - [T/T_c(p)]^2\} \quad \dots (1)$$

where $H_0(p)$ is the critical field at the absolute zero, and $T_c(p)$ the critical temperature at pressure p . The plot of $H_c(p)$ against T^2 should therefore be approximately a straight line. Similarly a plot of $\Delta H_c = H_c(0) - H_c(p)$ against T^2 should yield a straight line.

Figure 3 shows a graph of $H_c(p)$ against T^2 for aluminium with $p = 0$ and $p = 1,700 \pm 100$ atm. There appears to be some deviation from the linear behaviour predicted

by equation (1). This happens in many superconductors, but is surprising in this case since Goodman and Mendoza¹² found that equation (1) is obeyed to better than 1 per cent for $p = 0$. Our temperature determination may be less accurate than theirs, and this point requires further investigation.

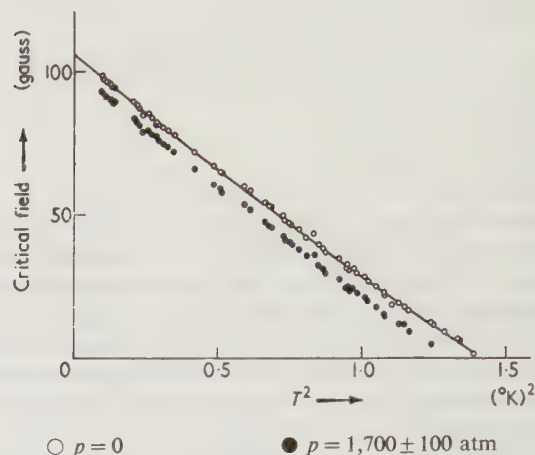


Figure 3. The critical field of aluminium

Figure 4 shows ΔH_c for two pairs of aluminium specimens and for two pairs of zinc specimens. Three to four demagnetizations were made with each pair of specimens. The relative accuracy in ΔH_c is lower than in H_c , and possible deviations from a linear dependence of ΔH_c on T^2 cannot be seen. The pressures in the ice-bomb were approximately equal in all runs, i.e. $p = 1,700 \pm 100$ in all cases.

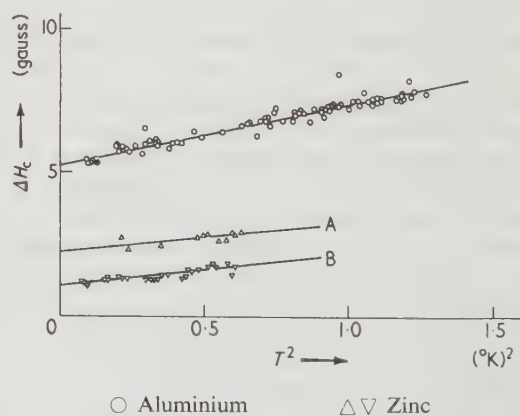


Figure 4. ΔH_c in aluminium and zinc; $p = 1,700 \pm 100$ atm in all cases

One pair of aluminium specimens was made from spectroscopically pure material obtained from Johnson Matthey and Co. Ltd. The other pair was made from zone-refined material. (We are grateful to Dr. W. Rohner of the Research Laboratory of the Aluminium Industrie A.G., Neuhausen, for making this available to us.) In both cases the specimens were drawn to size and left unannealed. In

aluminium the same values of ΔH_c were obtained in all runs, and a definite value for $\partial H_c/\partial p$ can be given. We find

$$\partial H_c/\partial p = -[3.1 \pm 0.2 + (1.7 \pm 0.2)t^2] \times 10^{-9} \text{ gauss dyn}^{-1} \text{ cm}^2$$

where $t = T/T_c$.

All the zinc specimens were cast from spectroscopically pure material from Johnson Matthey and Co. Although the results on ΔH_c obtained for each pair of specimens are consistent, and can be plotted as a linear function of T^2 , different specimen pairs give different values of ΔH_c . We believe that this must be caused by the presence of anisotropic stress systems within the ice-bomb, and that each set of results corresponds to a different stress system. If the width of the transition can be used as a guide then the results on curve A may perhaps be thought to correspond to the most nearly hydrostatic pressures. This curve yields for zinc

$$\partial H_c/\partial p = -[1.4 \pm 0.3 + (0.4 \pm 0.2)t^2] \times 10^{-9} \text{ gauss dyn}^{-1} \text{ cm}^2$$

Curve B gives

$$\partial H_c/\partial p = -[0.6 \pm 0.2 + (0.5 \pm 0.2)t^2] \times 10^{-4} \text{ gauss dyn}^{-1} \text{ cm}^2$$

On one occasion, badly smeared-out positive values for $\partial H_c/\partial p$ in zinc were obtained.

In cadmium, our results agreed with those of Alekseevskii and Gaidukov¹⁰ in some runs. In others we found a change in critical field three times smaller than theirs. Presumably, then, $\partial H_c/\partial p$ depends on the orientation of the stress in this metal too.

It is obviously possible to calculate the pressure dependence of T_c from these measurements, and we have pointed out elsewhere¹³ that $\partial \gamma/\partial p$ may be calculated, too. (γT is the electronic specific heat per mole.) If $H_c = H_0 \cdot f(t)$, where $t = (T/T_c)$, and if the form of $f(t)$ is independent of pressure, then

$$\begin{aligned} \frac{\partial H_c}{\partial p} &= \frac{\partial H_0}{\partial p} [f(t) - tf'(t)] + \\ &+ \frac{1}{2} H_0 t f''(t) \left[\frac{1}{\gamma} \frac{\partial \gamma}{\partial p} + \frac{1}{v} \frac{\partial v}{\partial p} \right] \dots (2) \end{aligned}$$

where $f'(t)$ is the derivative of $f(t)$ with respect to t , and v is the molar volume. This may be expressed somewhat more usefully in the form

$$\frac{d \ln \gamma}{d \ln v} = -2 \left[\frac{(\partial H_c/\partial p)_{t=0}}{(\partial H_c/\partial p)_{t=1}} f'(1) + 1 \right] \frac{d \ln T_c}{d \ln v} + 1 \dots (3)$$

We denote the quantity $d \ln \gamma/d \ln v$ by g in the following. Clearly also

$$\frac{d \ln T_c}{d \ln v} = \frac{K}{T_c} \cdot \left(\frac{\partial H_c}{\partial p} \right)_{T=T_c} \left(\frac{\partial H_c}{\partial T} \right)_{T=T_c}^{-1} \dots (4)$$

where K is the bulk modulus.

In calculating g it is found that the results are sensitive to the value of $f'(1)$ used in equation (3). In the case of

aluminium, the measurements by Goodman and Mendoza indicate $f'(1) = -2$, while our work suggests that $f'(1) = -1.85$ may be possible. A final decision must await a better determination of the critical field curve of aluminium. The results of such calculations are collected in Table 1 together with values of $d \ln T_c/d \ln v$. For zinc, both curves A and B shown in Figure 4 have been used.

Table 1

	$\frac{d \ln T_c}{d \ln v}$	$\frac{d \ln \gamma}{d \ln v} \equiv g$
Aluminium:		
Muench	12 ± 1	—
Grenier	13 ± 1	—
This work: $f'(1) = -2.0$	17 ± 1	10 ± 3
This work: $f'(1) = -1.85$		7 ± 3
Zinc:		
Curve A	6 ± 1	7 ± 3
Curve B	4 ± 1	1 ± 3

The probable errors are estimated from the scatter in our points. This does not exclude the possibility of systematic errors, and it appears¹ that higher values of g are obtained from direct measurements of $\partial H_c/\partial p$ than from measurements of the volume change on destruction of superconductivity. White¹⁴ has recently used the thermal expansion coefficient at low temperatures to determine g in aluminium. He finds a smaller value for g than either of those suggested here. (We are very grateful to Dr. G. K. White for informing us of the results of preliminary measurements.)

The measurements are of interest from two points of view. The volume dependence of γ gives information on the behaviour of the density of states $N(0)$ per mole per unit range of energy at the Fermi surface in the normal metal since

$$\gamma T = \frac{2}{3} \cdot \pi^2 k^2 N(0) T \dots (5)$$

where k is Boltzmann's constant. The volume dependence of T_c , on the other hand, is closely connected with the behaviour of the interaction which causes superconductivity. We will discuss these points separately.

The density of states

For a system of free electrons, $N(0)$ is given by

$$N(0) = \frac{2\pi m v}{h^2} \left(\frac{3n}{\pi} \right)^{1/3} \dots (6)$$

where m is the electronic mass, n the number of electrons per cubic centimetre, and v the molar volume of the metal. This clearly leads to

$$g \equiv d \ln N(0)/d \ln v = \frac{2}{3} \dots (7)$$

The values found for g in the present work, just as those found for other metals, are much larger than $\frac{2}{3}$. This is perhaps not surprising in view of the complicated structure of most of the metals investigated. Yet it must be noticed that $d \ln N(0)/d \ln v$ differs much more from the free electron value than $N(0)$ itself does.

This problem has recently been discussed by Rohrer.¹⁵ He showed that small regions of overlap of the Fermi surface from one Brillouin zone into another give contributions to $N(0)$ which are very sensitive to changes in the energy gap at the zone boundary. This energy gap itself depends upon the interatomic distance.

In the case of aluminium, Harrison⁵ has pointed out that the free electron model leads to a full first zone, a second zone almost full of holes, and a third zone with a somewhat complicated region of occupied states. In the fourth zone, too, there are minute occupied regions. The first zone, therefore, contributes nothing to $N(0)$. The second zone roughly 80 per cent and the third 20 per cent to the total value of $N(0)$, while the pockets in the fourth zone might contribute about 1 per cent.

More detailed calculations by Harrison,⁵ taking the effect of the periodic potential better into account, confirm that the first zone is full. (This disagrees with earlier views due to Heine.³) It appears, however, that the pockets in the fourth zone disappear. The area of the second zone surface is almost unaffected, while that in the third zone appears to be increased by the improved approximation. The area in this third zone is particularly sensitive to changes in the periodic potential since much of the surface lies very close to zone boundaries. It must be this surface which contributes to our large value of g .

In a quadrivalent metal with the same crystal structure, the overlap into the third zone is much bigger, and the area of Fermi surface in the third zone should be much less sensitive to changes in periodic potential. Thus we would expect a smaller contribution to g from the third zone in a quadrivalent metal than in a trivalent one (for a given row in the periodic table). Therefore, unless large contributions are made by the fourth zone or unless this argument is invalidated by the large difference in atomic number we might expect that in a substance such as lead g should be smaller than in aluminium. Unfortunately, the available experimental data is not yet sufficiently reliable to test conclusions of this sort. For aluminium the present work gives $g \simeq 8$. Until recently the corresponding value for lead was $g \simeq 2$, thus supporting the discussion above. Now, however, very careful work on lead by Mapother and Garfinkel¹⁶ has suggested $g \simeq 6$ in lead.

Our results on zinc show that in this metal, too, the density of states is strongly affected by a change in volume. It is interesting to note that recent work by Dmitrenko, Verkin, and Lazarev¹⁷ on the de Haas-van Alphen effect under pressure shows remarkable changes in the period of the observed oscillations. This corresponds to a rapid change in size of the pockets of charges giving rise to these oscillations. These pockets may thus be important in contributing to the observed high value of g .

The transition temperature

Bardeen, Cooper, and Schrieffer¹⁸ give an expression for the transition temperature T_c of a superconductor. This may be written in the form

$$T_c = 0.85 \theta_D \exp[-1/N(0)V] \quad \dots (8)$$

where θ_D is the Debye temperature, $N(0)$ is the density of states at the Fermi surface at $T = 0$, and V is an interaction constant which determines the strength of the interaction causing superconductivity. On examining the result of a volume change, we find

$$\frac{d \ln (T_c / \theta_D) / d \ln v}{\ln (0.85 \theta_D / T_c)} = \frac{d \ln (N(0)V)}{d \ln v} \quad \dots (9)$$

It is obviously of interest to investigate the effect of volume change on $N(0)V$, and this has been done theoretically by Pines¹⁹ and by Morel.²⁰ It might be thought that this would be closely correlated with the volume dependence of $N(0)$ itself, and Morel's work tends to support this conclusion. Pines, on the other hand, obtains an expression for $N(0)V$ which depends only on the valency and interatomic distance in the metal. He suggests that changes in $N(0)$ should be compensated by changes in V . In this case $d \ln N(0)V / d \ln v$ should not be correlated with g . This is supported by an observation of Rohrer¹⁵ who finds that

$$d \ln N(0)V / d \ln v \simeq 2$$

for most soft superconductors. The mutual compensation of changes in $N(0)$ and in V is especially clearly seen in a plot against g of all observations at present available of $d \ln N(0)V / d \ln v$ in soft superconductors. This is shown in Figure 5.

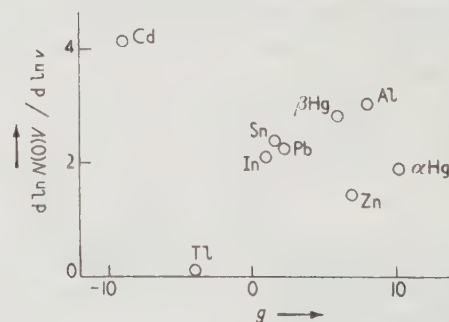


Figure 5. $d \ln N(0)V / d \ln v$ and its dependence on g in the soft superconductors

We are grateful to Professor Dr. P. Grassmann, the Director of this Institute, for his constant interest and support. We would also like to thank Dr. Rohrer for many interesting discussions, Dr. Lüthi for his aid at one stage of the experimental work, and Mr. P. Wyder for carrying out a number of computations for us on the ERMETH (Elektronische Rechenmaschine der ETH). This work was supported in part by the Arbeitsbeschaffungsfonds des Bundes.

REFERENCES

1. For a review see OLSEN, J. L., and ROHRER, H. *Helv. phys. acta* **33** (1960)
2. GUNNERSON, E. M. *Phil. Trans.* **A249**, 299 (1957)
3. HEINE, V. *Proc. roy. Soc.* **A240**, 361 (1957)
4. HARRISON, W. A. *Phys. Rev.* **116**, 555 (1959)
5. HARRISON, W. A. *Phys. Rev.* **118**, 1182 (1960)
6. GRENIER, C. *Thesis*, Paris (1956)
7. MUENCH, N. L. *Phys. Rev.* **99**, 1814 (1955)
8. ANDRES, K. A. Private communication
9. LAZAREV, B. G., and KAN, L. S. *J. Phys., Moscow* **8**, 193 (1944)
10. ALEKSEEVSKII, N. E., and GAIDUKOV, Y. P. *J. exp. theor. Phys.* **29**, 898 (1955)
11. OLSEN, J. L. *Helv. phys. acta* **32**, 310 (1959)
12. GOODMAN, B. B., and MENDOZA, E. *Phil. Mag.* **42**, 594 (1951)
13. OLSEN, J. L., and ROHRER, H. *Helv. phys. acta* **30**, 49 (1957)
14. WHITE, G. K. Private communication
15. ROHRER, H. *Helv. phys. acta*. In press
16. MAPOTHER, D. E. Private communication
17. DMITRENKO, I. M., VERKIN, B. I., and LAZAREV, B. G. *J. exp. theor. Phys.* **35**, 328 (1960)
18. BARDEEN, J., COOPER, L. N., and SCHRIEFFER, J. R. *Phys. Rev.* **108**, 1175 (1957)
19. PINES, D. *Phys. Rev.* **109**, 280 (1958)
20. MOREL, N. J. *Phys. Chem. Solids* **10**, 277 (1959)

EDITORIAL NOTE

As a service to our authors, the price of reprints has been reduced. The new schedule can be found on the inside back cover. We are aware that reprints of published papers are of great importance to authors and we are making every effort to provide these as cheaply as is compatible with a high standard of printing.

Studies of the Low Temperature Distillation of Hydrogen Isotopes

T. M. Flynn National Bureau of Standards, Boulder, Colorado

Received 9 September 1960

THE merits of producing deuterium by the distillation of hydrogen are quite well known. However, the best methods of distillation column design are not so well established.

The usual correlations available for predicting column design parameters fail when applied to the hydrogen systems, since the bulk of the data for the correlations is obtained from higher boiling systems such as aqueous solutions and hydrocarbons. For example, the optimum downcomer area was found to be much larger than predicted, and one well known correlation¹ gives an overall plate efficiency of 130 per cent.

These and other correlations are generally applicable only to systems having physical characteristics similar to those for which the data were obtained. The unconventional properties of liquid hydrogen, which has a density one-fourteenth, and a viscosity one-twentieth that of boiling water, give rise to unusual behaviour in a distillation column. Accordingly, research has been conducted at the National Bureau of Standards Cryogenic Engineering Laboratory in Boulder, Colorado, to determine the design parameters for a hydrogen distillation column.

Since the behaviour of packed columns²⁻⁵ and bubble cap columns⁶ has been previously reported, this research was primarily concerned with the characteristics of perforated or sieve plate columns. Such parameters as plate spacing, plate geometry, maximum allowable vapour velocity, weir height, and downcomer area were investigated, and the results of these investigations were applied to the design of a pilot plant column.

Since deuterium occurs naturally in the form of HD rather than D₂, the pilot plant was designed to separate the system H₂-HD. However, all the experimental work leading to the design of the pilot plant was carried out with the H₂-D₂ system, for D₂ is readily available, and HD is not. The use of the H₂-D₂ system in the experimental work rather than the H₂-HD system is easily justified. Since the two pairs have very similar physical properties, they should have similar distillation behaviour. As an index for comparison, the Drickamer and Bradford¹ correlation predicts that the two systems will have the same overall plate efficiency. The O'Connell⁷ correlation predicts a plate efficiency for the HD system only slightly higher than that for the D₂ system.

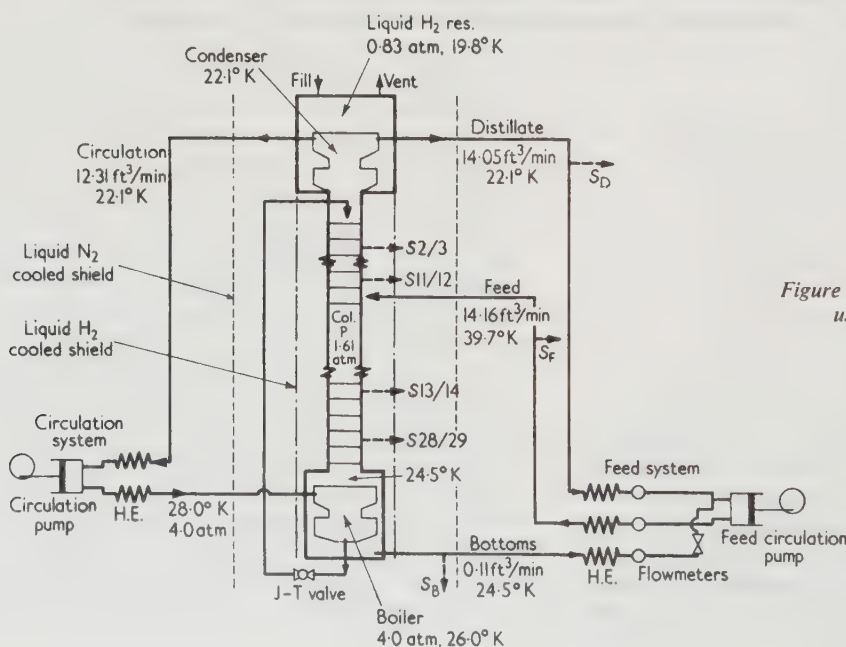


Figure 1. A schematic flow diagram of pilot plant used for low temperature distillation

The initial distillation work was done with a series of 1.5 in. O.D. columns (1.35 in. I.D.), and the results of these preliminary experimental studies have already been published.⁸ These studies culminated in the design and operation of a hydrogen distillation pilot plant. The design of this plant was covered in the same article,⁸ and some details of its operation have also been reported.⁹ However, the observed plate efficiencies have not been satisfactorily explained. This is the subject of the present paper.

The pilot plant column

The pilot plant column contains thirty plates 6 in. in diameter spaced 4 in. apart, and made of 40 mesh brass screen. Maximum feed rate is 14.2 ft³(n.t.p.)/min. The column was operated with vapour velocities ranging from 0.2 to 2.0 in./sec, and reflux ratios from total to an (L/D) of 2.05. A schematic diagram of the column is shown in Figure 1. A set of data typical of a partial reflux run is recorded in Table 1. For details of the design and operation consult the previous articles.^{8,9}

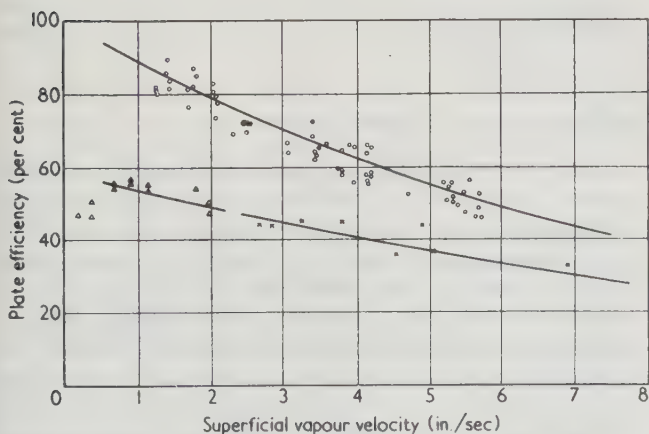
Experimental results

The column has been operated repeatedly with hydrogen for periods of 1–5 days of continuous operation. The most interesting information obtained from these runs concerns the plate efficiency.

Overall plate efficiency

The principal object of experimental runs was to determine the overall plate efficiency. Sample taps, located at seven points along the column (Figure 1), fed gas phase samples to a continuously recording thermal conductivity analyser.¹⁰ These analyses were recorded along with the other process variables so that the overall plate efficiency could be determined as a function of vapour velocity. This dependence is shown in Figure 2.

These plate efficiencies represent data for runs during which the reflux ratio was varied from total to an (L/D)



○ 1.35 in. columns, sieve plates △ 6.00 in. column, sieve plate
× 1.06 in. column, bubble cap (Sellers and Augood)

Figure 2. Plate efficiencies of three types of column

ratio of 2.05, and during which the composition of the mixtures on the plates varied from pure hydrogen to 98 per cent deuterium in hydrogen. No dependence of overall efficiency on either reflux ratio or composition could be found.

Three points at low vapour velocity, from 0.1 to 0.5 in./sec, group themselves around a low value of plate efficiency. This behaviour at low vapour velocities is not uncommon, and has been reported by several authors^{11, 12} who investigated higher boiling systems. The effect is one of hydraulics on the plate, and not one due to peculiarities of a given system. It is therefore reasonable to expect to find this behaviour even in the hydrogen system.

Two sets of data, in addition to the pilot plant efficiencies, are shown in Figure 2. One set is that of Sellers and Augood,⁸ which was obtained with a single bubble cap in a 27 mm diameter column. This set correlates very well with that of the pilot plant.

The other data of Figure 2 is that obtained from the 1.35 in. diameter columns. These plate efficiencies are significantly higher than those of the pilot plant and of Sellers and Augood. This curious discrepancy will now be examined.

Plate efficiency relations

On a theoretical plate, by definition,^{13, 14} the average composition of the vapour leaving is the equilibrium value for the liquid leaving. The customary index of comparison between actual behaviour and the theoretical, or ideal, behaviour is efficiency. There are several forms of plate efficiency, which may be related in various ways. It is important, therefore, to define plate efficiency, and to realize which of the plate efficiencies are measured under particular experimental conditions.

Overall plate efficiency E°

One of the most useful forms of plate efficiency is due to Lewis,¹³ the overall plate efficiency E° . It is defined as the ratio between the number of theoretical plates necessary to effect a given separation and the number of actual plates required for the same separation. This overall plate efficiency has, in itself, no fundamental mass transfer basis, but is still quite useful since only terminal conditions are required for its application.

Murphree point efficiency E'_{mv}

The Murphree point efficiency E'_{mv} was derived by Murphree,¹⁴ who assumed a simplified expression for the instantaneous mass transfer to one bubble of vapour rising through the liquid. The derivation assumes that the vapour composition in the bubble changes continuously by mass transfer, and that the bubble is rising through a liquid of constant composition. It is defined as:

$$E'_{mv} = \frac{Y'_i - Y'_o}{Y'_i - Y_e} \quad \dots (1)$$

where Y'_i is the local mole fraction of the more volatile

component in the bubble entering the liquid, Y'_o is the local mole fraction composition of the bubble leaving the liquid, and Y_e is the mole fraction composition of the vapour in equilibrium with the liquid of uniform composition on the plate.

Murphree¹⁴ has also shown that E'_{mv} may be expressed as

$$E'_{mv} = 1 - \exp(-m) \quad \dots (2)$$

where

$$m = \frac{PK_G A \theta}{G} \quad \dots (3)$$

and P is the total pressure, K_G is the overall mass transfer coefficient, A is the interfacial area of the bubble, θ is the contact time, and G is the moles of gas in the bubble.

In many cases there are considerable differences in the composition of the liquid at various points on the plate. In these instances, E'_{mv} applies as derived for any point on the plate, but not for the whole plate.

Murphree plate efficiency E_{mv}°

The conditions necessary for the proper application of E'_{mv} may not be met under the defined experimental conditions. However, it is still convenient to have a form of efficiency similar to E'_{mv} , but defined for the plate as a whole. This form is known as the Murphree plate efficiency E_{mv}° , and is defined:

$$E_{mv}^\circ = \frac{Y_i - Y_o}{Y_i - Y_e^*} \quad \dots (4)$$

where Y_i and Y_o are the average composition of the vapour entering and leaving the plate, respectively, and Y_e^* is the composition of the vapour in equilibrium with the liquid leaving the plate.

The equations for E'_{mv} and E_{mv}° appear similar, but the former uses values for a small region of the plate, while the latter uses average values. In general, E_{mv}° may be considered the integrated effect of all the E'_{mv} values on the plate.

Relation between E° and E_{mv}°

Lewis¹⁵ has shown a relation between the overall column efficiency E° and the Murphree plate efficiency E_{mv}° . This relation is

$$E^\circ = \frac{\ln[1 + E_{mv}^\circ(\lambda - 1)]}{\ln \lambda} \quad \dots (5)$$

where

$$\lambda = \frac{KV}{L}$$

and K is the equilibrium constant (Y/X), V is the vapour rate, and L is the liquid rate.

This relation is correct provided that: (1) L/V is constant; (2) the equilibrium line is straight, $Y_e = KX + b$; and (3) E_{mv}° is the same for all plates considered.

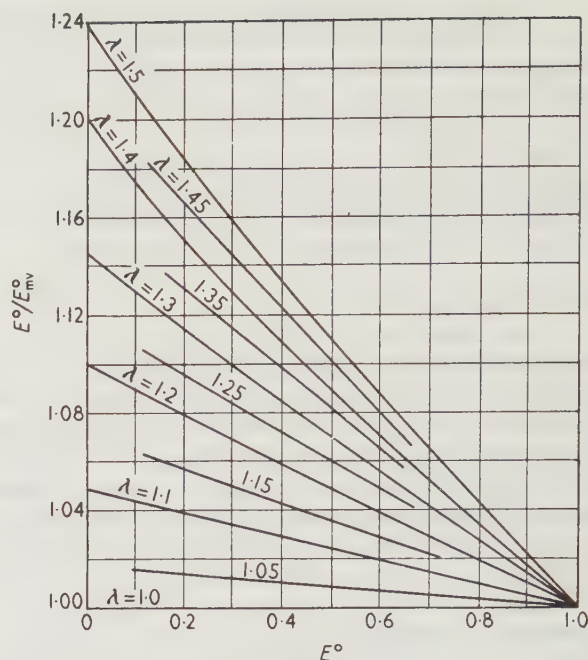


Figure 3. Overall plate efficiency E° versus Murphree plate efficiency E_{mv}°

Equation (5) is presented graphically in Figure 3. It can be seen that as long as (KV/L) is close to 1.00, E° and E_{mv}° differ by only a few per cent.

In the work with the small diameter columns, the ratio (KV/L) was close to 1.0, and hence there should be no significant difference between values of E° and E_{mv}° . The validity of this conclusion can be seen in Figure 4, where plate efficiencies of the 1.35 in. diameter columns previously shown in Figure 2 are plotted against vapour velocity. The number of plates for which the efficiency was measured is now given as the parameter. Those values for one plate should correspond to E_{mv}° . Those values for two, three, and four plates should correspond to E° . There is apparently no significant difference between the several sets of efficiencies, indicating that E° and E_{mv}° are approximately the same.

Relation between E_{mv}° and E'_{mv}

On the theoretical plate, the average composition of the vapour leaving is the equilibrium value for the liquid leaving. If the vapour and liquid on a plate were completely mixed, it would be impossible to obtain a better separation than that given by a theoretical plate, and the value of E_{mv}° approaches that of E'_{mv} . However, when there is a composition gradient in the liquid across the plate, the average concentration of the more volatile component on the plate may be greater than the concentration of the liquid leaving the plate. As a result of this greater concentration, the vapour actually leaving the plate may have a concentration greater than that in equilibrium with the liquid leaving the plate.

It is thus possible for this concentration gradient effect to give E° (and hence E'_{mv}) values greater than the E'_{mv} values, since such gradients do not apply to the E'_{mv} values.

Lewis¹⁵ also considered the effect of several experimental conditions, assuming (1) E'_{mv} was constant across the plate, and (2) $Y_e = KX + b$. For complete vapour mixing, but negligible liquid mixing on each plate, Lewis derives

$$E'_{mv} = \frac{\exp(E'_{mv}\lambda) - 1}{\lambda} \quad \dots (6)$$

Figure 5 presents equation (6) graphically, with $\lambda = (KV/L)$ as the parameter. It can be seen that, under the condition of liquid non-mixing described, the values of E'_{mv} (and hence E°) can exceed the values of E'_{mv} significantly.

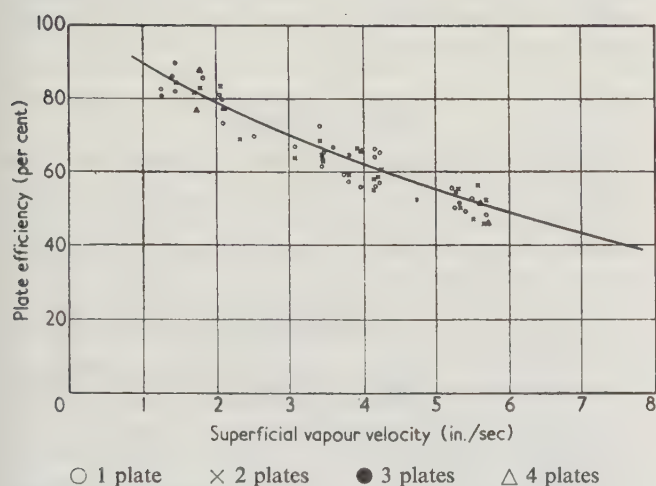


Figure 4. Plate efficiency; number of plates as the parameter (1.35 in. columns, sieve plates)

Discussion of experimental results

Figure 2 indicated that the plate efficiencies measured in the small columns were considerably larger than those of the pilot plant and those of Sellers and Augood. In the small columns, the weirs were directly opposite one another, so that the liquid had a direct and unobstructed path. In this case, it is possible that the liquid was able to flow directly across the plate with little or no mixing. Hence the efficiencies measured would correspond to values of E'_{mv} (or E°) and not to E'_{mv} .

In the pilot plant column, the downcomers were adjacent to one another, separated by a weir. This arrangement caused a semicircular liquid path which tends to induce a more complete liquid mixing.

In the columns of Sellers and Augood,⁶ the liquid path was interrupted by a bubble cap, which undoubtedly caused complete liquid mixing.

Since complete liquid mixing occurred in the columns of Sellers and Augood, and since their data fits that of the pilot plant column, the case for complete mixing in the pilot plant column is reinforced. In these instances, the

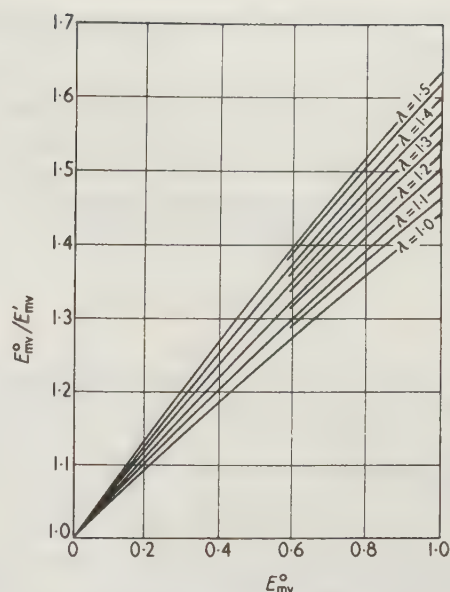


Figure 5. Plate efficiency E'_{mv} versus point efficiency E'_{mv}

efficiencies measured would correspond to values of E'_{mv} . Figure 6 illustrates this argument.

In Figure 6, the best curve of the plate efficiency data from the small diameter column is repeated from Figure 2 as the dashed line. The best curve of the data from the pilot plant column and from Sellers and Augood is repeated from Figure 2 as the solid line.

The points in Figure 6 are the result of treating the data from the small columns by means of equations (5) and (6). In this treatment, it was assumed that this data actually represented E'_{mv} (or E°), corresponding to incomplete liquid mixing. Then equation (6) was applied to determine the corresponding E'_{mv} value for complete mixing. The data treated in this manner is seen to correspond quite well with

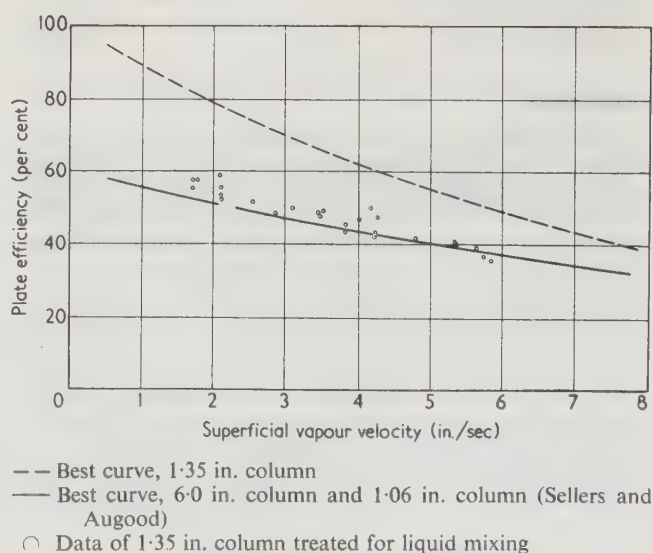


Figure 6. Plate efficiencies of the 1.35 in. columns treated for liquid non-mixing

the experimental curves of the pilot plant and of Sellers and Augood.

The results of this treatment, as presented in Figure 6, offer a strong argument for the case of incomplete mixing in the small columns, and for complete mixing in the pilot plant and in the columns of Sellers and Augood. In the former case, the efficiencies actually measured correspond to E'_{mv} (or E°), and in the latter cases to E'_{mv} .

Table 1. Data of typical run

Flow Rates		
Stream	(ft ³ (n.t.p.)/min)	(g.moles/min)
Bottoms	0.11	0.14
Feed	14.16	17.89
Distillate	14.05	17.75
Circulation	12.31	15.55
Pressure, absolute		
Point	(atm)	
Circulation (interior of reboiler)	4.0	
Column (exterior of reboiler)	1.61	
Hydrogen reservoir	0.83	
Temperature		
Point	(°K)	
Bottoms (exterior of reboiler)	24.5	
Feed (into the column)	39.7	
Distillate (top of column)	22.1	
Circulation		
(into reboiler)	28.0	
(interior of reboiler)	26.0	
Hydrogen reservoir	19.8	
Analyses		
Sample	Composition (mole % D ₂)	
Bottoms	96.9	
Feed	0.77	
Distillate	0.015	
Circulation	0.015	
Between plates 28/29	87.0	
Between plates 13/14	1.0÷	
Between plates 11/12	1.0—	
Between plates 2/3	0.035	

Conclusions

A few conclusions may be inferred from this analysis. The first is that plate efficiency is not *per se* a function of the column diameter, as might have been supposed.

Instead, the plate efficiency depends upon the degree of liquid mixing. If this mixing is complete, the efficiency is invariant with respect to plate diameter.

On the small diameter perforated plates, it is possible to have incomplete mixing, corresponding to a higher value of apparent efficiency.

It should be possible to obtain higher values of plate efficiencies in hydrogen distillation columns by inhibiting the liquid mixing, since the E° (or E'_{mv}) values are higher than the E'_{mv} values. The feasibility of this suggestion depends at least upon the arrangement of the weirs and downcomers, the column diameter, the vapour and liquid rates, and the mass transfer liquid mixing length. Nevertheless, this suggestion may prove attractive.

The comparison of efficiencies indicates that efficiency does not depend strongly upon the type of plate. Since the efficiency of perforated and bubble cap plates is much the same, the choice of plate depends more strongly on the plate hydraulic characteristics.

REFERENCES

1. DRICKAMER, H. G., and BRADFORD, J. R. *Trans. Amer. Inst. chem. Engrs* **39**, 319 (1943)
2. ABRAHAM, B. M., and FLOTOW, H. E. *ANL-5204* (Argonne National Laboratory, Illinois)
3. FOOKSON, A., POMERANTZ, P., and ROTHBERG, S. *J. Res. nat. Bur. Stand.* **47**, 449 (1951)
4. ROTH, E., STOULS, L., DIRIAN, G., LAZARD, B., and NIEF, G. *Proc. 2nd Int. Conf. Peaceful Uses of Atomic Energy*, Vol. 4, p. 449 (U.N.O., 1958)
5. FLYNN, T. M., TIMMERHAUS, K. D., WEITZEL, D. H., and DRAPER, J. W. *Advances in Cryogenic Engineering*, Vol. 3, pp. 58-63 (Plenum, New York, 1960)
6. SELLERS, E. S., and AUGOOD, D. R. *Trans. Instn chem. Engrs, Lond.* **34**, 53 (1956)
7. O'CONNEL, H. E. *Trans. Amer. Inst. chem. Engrs* **42**, 741 (1946)
8. TIMMERHAUS, K. D., WEITZEL, D. H., and FLYNN, T. M. *Chem. Engng Progr.* **54**, No. 6, 35 (1958)
9. FLYNN, T. M. *Chem. Engng Progr.* **56**, No. 2, 37 (1960)
10. PURCELL, J. R., DRAPER, J. W., and WEITZEL, D. H. *Advances in Cryogenic Engineering*, Vol. 3, pp. 191-195 (Plenum, New York, 1960)
11. PEAVY, C. C., and BAKER, E. M. *Industr. Engng Chem. (Industr.)* **29**, 1056 (1937)
12. PERRY, J. H. (Ed.). *Chemical Engineers' Handbook*, 3rd Ed. (McGraw-Hill, New York, 1950)
13. LEWIS, W. K. *Industr. Engng Chem. (Industr.)* **14**, 492 (1922)
14. MURPHREE, E. V. *Industr. Engng Chem. (Industr.)* **17**, 747 (1925)
15. LEWIS, W. K. *Industr. Engng Chem. (Industr.)* **28**, 399 (1936)

Cooling by Adiabatic Magnetization of Superconductors

M. Yaqub *Clarendon Laboratory, Oxford*

Received 6 August 1960

IN 1932 Keesom and Kok¹ investigated the specific heat anomaly at the superconductive transition point of tin. Two of their values, however, differed widely from the rest and this was ascribed to the accidental presence of a small magnetic field. On the basis of this observation, Mendelssohn suggested that the adiabatic transition between the superconductive and the normal state might be accompanied by a magneto-caloric effect which could be used for obtaining low temperatures. Magnetization experiments on tin by Mendelssohn and Moore² demonstrated the existence of this effect and small coolings ($\sim 0.3^\circ\text{K}$) were, in fact, observed. This result was confirmed by Keesom and Kok³ who obtained coolings of the order of 0.15°K in thallium. A somewhat improved arrangement⁴ yielded final temperatures of the order of 0.2°K which were estimated from an extrapolation of the critical field curve of tin to low temperatures. It was decided, prior to the development of the cooling method, to measure more carefully the critical fields of a number of superconductors which might serve as cooling agents. This work⁵ was interrupted by the war. Work on adiabatic magnetization was not resumed until 1954 when the present series of experiments was started.

Thermodynamic considerations

All superconductors below their transition temperatures can be brought back to their normal state by the application of a strong enough magnetic field called the critical field H_c . H_c rises from zero at the transition temperature to a temperature independent value as we approach the absolute zero. Since the thermodynamics of the transition is analogous to any other phase transition, one can calculate the entropy differences in the two phases as

$$S_n - S_s = -\frac{H_c}{4\pi} \frac{dH_c}{dT} \quad \dots (1)$$

where S_n and S_s are the entropies in the normal and superconducting states, respectively. Since dH_c/dT is always negative, we have

$$S_n - S_s > 0$$

except when $H_c = 0$, or $dH_c/dT = 0$, i.e. at the transition temperature T_c and at the absolute zero where dH_c/dT must vanish as a consequence of the third law of thermodynamics.

The superconducting state, therefore, is a more ordered state of the metal and is due to a fraction of the conduction electrons going into a state of zero entropy below the transition temperature.⁶ The temperature-entropy curve, which is typical for a superconductor in both phases, is given in Figure 1. There are two electronic contributions S_n and S_s corresponding to the normal and superconductive states, and the contribution S_{lat} due to the lattice vibrations, which is common to both.

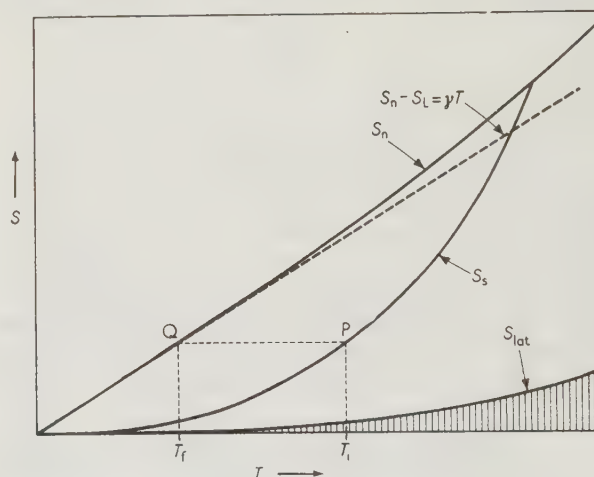


Figure 1. Diagram of entropy S versus temperature T curve

From equation (1) it is clear that in isothermal destruction of superconductivity by a magnetic field, heat will be absorbed, and, if the magnetization is carried out adiabatically, the temperature must fall. Thus a superconductor cooled in zero field to P will, when magnetized adiabatically, cool until it reaches Q where its entropy in the normal state is the same as in the superconducting state at P.

Corak, Goodman, Satterthwaite, and Wexler⁷ and Goodman⁸ have shown from calorimetric measurements that, well below the transition temperature, the electronic contribution to the atomic heat in the superconducting state can be represented by

$$C_{es}(T) = \gamma T_c a \exp\left(\frac{-bT_c}{T}\right) \quad \dots (2)$$

where γ is the electronic specific heat coefficient in the normal state, T_c the transition temperature, and a and b are constants depending on the metal. The above expression has also been derived theoretically by Bardeen, Cooper, and Schrieffer⁹ suggesting $a \approx 8.5$ and $b \approx 1.44$ for all superconducting metals. From equation (2) we can calculate the cooling ideally obtainable by equating the entropies in the two phases. The relation between the initial temperature T_i and the final temperature T_f obtained on magnetization is

$$\gamma T_c a \int_0^{T_i} \frac{\exp(-bT_c/T)}{T} dT + \frac{A}{3} \frac{T_i^3}{\Theta^3} = \gamma T_f + \frac{A}{3} \frac{T_f^3}{\Theta^3} \quad \dots (3)$$

where Θ is the Debye characteristic temperature of the metal and A has the value 464.4. In this way, by calculating T_f for various values of T_i we have plotted curves showing the relation between the initial and final temperatures for tantalum and tin (Figure 2). From these curves we see that starting from 1.25°K, final temperatures of 0.05°K and 0.1°K can be attained on magnetizing tantalum and tin, respectively.

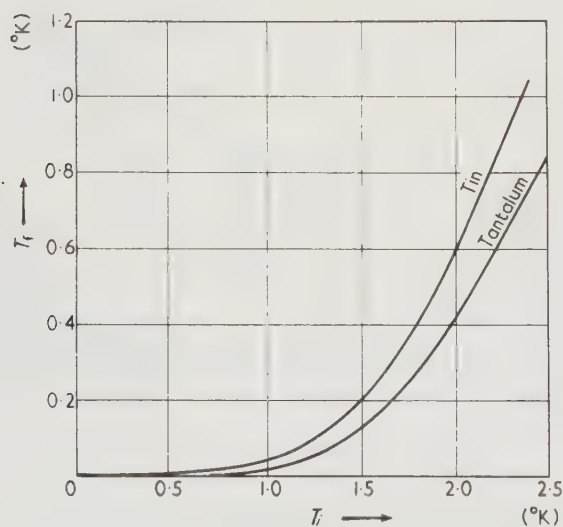


Figure 2. Diagram showing the relation between the initial and final temperatures for tantalum and tin

Advantages and disadvantages of the method

Comparing this method with the adiabatic demagnetization of paramagnetic salts, we find that it has certain disadvantages. The most important of these is the linear fall with temperature of the specific heat leading to low absolute values near 0.1°K. This makes the cooling efficiency in this region, measured in calories per cubic centimetre, much smaller than that for paramagnetic salts, and although fairly large temperature drops may be effected, it will be difficult to maintain the lowest obtainable temperatures for any length of time. The smallness of

the entropy changes near 0.1°K also makes this process relatively inefficient for cooling appreciable quantities of other substances.

Another aspect which tends to reduce the efficiency of this method is the production of irreversible Joule heat. During the process of magnetization the specimen traverses the intermediate state and a change of field with time induces eddy currents in the normal regions whose dying out causes heating of the specimen. Consequently, unless the rate of increase of the field is very slow, the temperature drop may be considerably less than that calculated from equation (3).

There are, however, several points in favour of this method. For instance, the necessary fields to destroy superconductivity are of the order of a kilo-oersted or less for all superconductors and can be easily produced over large volumes. One can, therefore, magnetize considerable quantities of a metal and in this way compensate, to some extent, for the smallness of the heat capacity. Another attractive feature of the method is the comparatively large thermal conductivity of metals below 1°K.¹⁰ Near 0.05°K metals have a conductivity twenty times larger than that of paramagnetic salts.¹¹ This fact coupled with the small heat capacity makes the equilibrium times very small. The presence of a metal also makes it easier to make thermal contacts, and specimens to be investigated can be directly soldered to the refrigerant metal.

It appears that the method would be particularly useful in the temperature range between 0.3 and 1°K. Most paramagnetic salts in common use have specific heat maxima below 0.3°K and their heat capacities between 0.5 and 1°K are rather small. On account of the fact that, due to gas desorption, vacuum conditions begin to deteriorate above 0.6°K, work with them becomes increasingly difficult above this temperature. Moreover, the specific heat of the salts fall with rise in temperature and this accelerates the warming-up rates. In the superconducting method, on the other hand, the entropy of the final phase is rising linearly with absolute temperature and the rate of warming-up gets retarded by the steadily increasing heat capacity.

The choice of the metal

Metals with a high Debye Θ , a high transition temperature, and a large coefficient of electronic specific heat γ , are particularly suitable as cooling agents. Since the amount of heat which has to be extracted from the metal to cool it from hydrogen to helium temperatures is inversely proportional to the third power of Θ and, since a fairly large quantity of the metal has to be used, a high value of Θ is desirable in order to reduce the quantity of liquid helium required for preliminary cooling. Tantalum and niobium satisfy these conditions, but the quantities required to cool a reasonable amount of any other substance (say 10 cm³ of liquid helium) to an appreciable degree is of the order of 25 moles, which was considered excessive for our purposes. Tin, on the other hand, is readily available in large quantities at a reasonable cost.

It was therefore decided to use tin, although it has a much smaller Debye Θ and, on account also of a smaller γ than that of tantalum and niobium, is not as good a cooling agent.

Apparatus

The apparatus had to be designed with the following essential features:

- (1) A large cryostat capable of accommodating and cooling about 40 moles of tin to a temperature of about 1° K;
- (2) A helium vessel surrounding this cryostat maintained at a temperature of about 1° K, so as to reduce the heat influx; and
- (3) A suitable thermometer to measure accurately the temperature in the range of about 0.1 to 1° K.

was necessary in order to facilitate the suspension and removal of the tin block which is held in position inside the cryostat by means of thin stainless steel wires. A small vessel V, made of thin walled copper, having a capacity of about 2 cm³ is soldered on the top of the tin specimen. By condensing a small quantity of liquid helium into this vessel and pumping it off vigorously, the temperature of the specimen could be lowered to 0.8° K before magnetization, while the outer helium bath was at 1.25° K. This procedure was adopted after the failure of a number of experiments, in which the specimen was cooled to 1.25° K by means of helium exchange gas. Then, magnetization after the vacuum space had been pumped for several hours resulted in no cooling at all, showing that the exchange gas could not be successfully pumped out at 1.25° K. Moreover, by pumping the helium in the vessel V the specimen could be magnetized from a lower initial temperature.

Temperature measurement

For measuring the temperature of the specimen we used 0.25 W LAB resistors T_1 and T_2 (Figure 3) with a nominal value of 33 Ω at room temperature. Their resistance varied from about 160 Ω at 4.2° K to about 2,000 Ω at 1.0° K, while their sensitivity defined as dR/RdT rose from approximately 0.5 at 1.0° K to above 10 at 0.2° K. A 24 s.w.g. enamelled copper wire was tightly wound round the carbon and a heavy layer of 'Araldite' was applied all round it to cover completely the body of the resistor. It was then baked until the 'Araldite' was set hard, giving a good thermal contact between the copper wire and the carbon. The loose ends of the copper wire were then soldered to the tin specimen. Thermometer resistance was measured by a Wheatstone bridge having equal ratio arms and, to cancel the lead resistance, a three-lead connection to the resistor was used.

Calibration of carbon resistance thermometers

The lowest temperature to which we could calibrate our thermometers with the above apparatus was 1.25° K measured by means of helium vapour pressure manometers. However, the range it was expected to cover by magnetizing tin was between 0.1 and 1° K and, therefore, calibration against a susceptibility thermometer below 1.25° K was necessary. In the early experiments the resistors were calibrated in a separate demagnetization cryostat and then attached to the specimen. It was found that the process of transferring from one cryostat to the other, which involved soldering, invariably changed their characteristics by about 3 per cent and in some cases errors of up to 15 per cent were introduced in temperature determinations. If, however, the resistors were left untouched in between experiments, their reproducibility remained within 1 or 2 per cent. Since the same arrangement was used for specific heat measurements, several experiments were made to see under what conditions maximum reproducibility could be achieved. It was found that if the

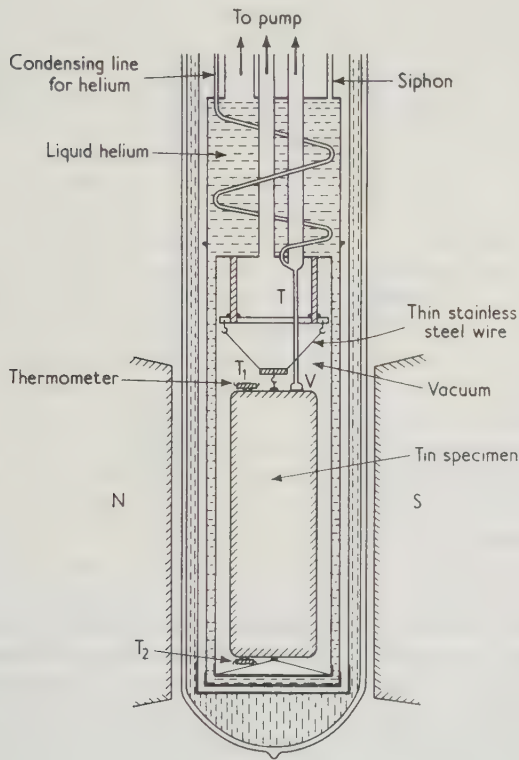


Figure 3. The apparatus

The apparatus in its final form is shown diagrammatically in Figure 3. It consists of a cylindrical brass cryostat 30 cm long and 8 cm in diameter which can hold a block of tin weighing 4.5 kg. The surrounding helium vessel with a total capacity of 800 cm³ was made up of two separate parts. The upper half consists of a copper vessel of 700 cm³ and the lower is made up of two concentric brass cylinders, the space between which contains the remaining 100 cm³ of helium. A composite helium vessel

following precautions were observed the thermometers were reproducible to better than 0.1 per cent:

- (1) The carbon of the thermometer was completely covered in 'Araldite' before baking, thus preventing moisture from condensing on the carbon during the experiments;
- (2) It was soldered to the specimen once and for all and left undisturbed from one experiment to another; and
- (3) The thermometers had to be cooled to helium temperatures from room temperature three or four times before calibrating.

Hence, it was necessary to calibrate the resistors against magnetic susceptibility in contact with the tin specimen so that they were left untouched between a calibration and a magnetization experiment. For this purpose an alternative set of vacuum cases and a helium vessel were designed which had appropriate tails at the bottom to accommodate the salt pill and the measuring coil. By demagnetizing the salt pill the temperature of the specimen could be lowered to 0.15°K and the thermometer resistance calibrated against the susceptibility of the salt. The cryostat with the salt pill in position and in thermal contact with the tin specimen is shown diagrammatically in Figure 4.

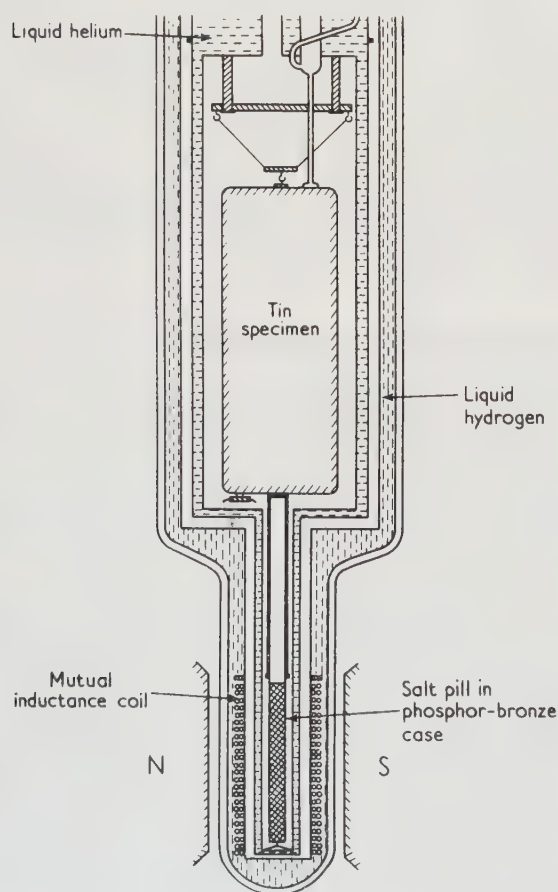


Figure 4. The cryostat with the salt pill in position

The magnetic field

For magnetizing the specimen a transverse field produced by a horseshoe type of electromagnet was used. It was capable of producing a field of about 1 kgauss. In the earlier experiments it was excited by a battery source and in the later, for technical reasons, by d.c. mains.

Experimental results and discussion

The specimen used in the early experiments was a cylindrical block of tin 15 cm long and 6.95 cm in diameter. It was supplied by the Tin Research Institute, London, and its purity as quoted by the suppliers was 99.990 ± 0.002 per cent. It was annealed at a temperature of 200°C for 2 weeks before magnetization.

Theoretically, the transition can be made isentropic only if the field is applied infinitely slowly. For practical purposes an order of magnitude calculation showed that, in order to keep the gain in entropy due to eddy current heating negligible, the magnetization would have to take several minutes. Since owing to the complicated geometry no exact calculations were possible, it was decided to study the effect of varying the rate of increase of the field. Results of the coolings obtained on applying a field of 305 gauss at various rates are given in Table 1.

Table 1

Time taken to apply the field (min)	Final temperature achieved (°K)
2	0.6
4	0.52
6	0.44
8	0.42
10	0.38
12	0.36
14	0.35
16	0.35

Increasing the time of application of the field beyond 16 min did not result in reaching a lower temperature, and 0.35°K was, in fact, the lowest obtained in this series of experiments. This is a good deal higher than the expected value of 0.02°K and shows that the magnetic heating caused by inducing the transition in a finite time is not the only factor responsible for reducing the temperature changes achieved on magnetization. Dolecek in his attempts to study the temperature-entropy relations of lead spheres has also found that the fall in temperature on adiabatic magnetization was considerably smaller, provided the temperature before magnetization was well below T_c . The reduced change in temperature could be caused by the following reasons.

(1) If, as is possible in a polycrystalline specimen of large dimensions, there exist regions of strain with high critical fields, then a fraction of the metal may remain superconducting and cause a higher final temperature. But the

fraction which would give a final temperature of 0.35°K is nearly 0.8 and is an impossibly high value. However, in order to make sure, experiments were repeated after annealing the specimen for a further period of 2 weeks at a temperature of 200°C, but no improvement was found.

(2) A well annealed specimen of pure tin is likely to have large flawless crystals which may superheat and cause eddy current heating independent of the rate of change of the field. Although no accurate measurements were made, evidence of superheating at the beginning of the transition was found on magnetizing an ellipsoid of pure tin with a known demagnetizing coefficient. Just before the field began to penetrate, the value of the field at the equator of the ellipsoid was 3 to 4 oersteds greater than the critical field H_c for the initial temperature.

(3) The process of increasing the field by reducing the resistance in the circuit of the electromagnet could not be made continuous by using an ordinary rheostat which changes its resistance in steps. Due to this, there would be a certain amount of Joule heating independent of the time taken to complete the transition. In order to reduce the heating due to this cause, subsequent experiments were performed on a laminated tin specimen which consisted of 300 circular disks of pure tin 0.5 mm thick and 6 cm in diameter. They were tightly packed in a brass cylinder and were insulated from each other by means of a thin layer of varnish. In order to improve thermal contact between the disks and the cylinder, the dead space was filled with helium at a pressure of 15 atm at room temperature. Magnetization of this composite specimen gave final temperatures considerably higher than 0.35°K. Besides, the time taken for preliminary cooling to 4.2°K was over 50 per cent longer than in the case of a solid cylinder. It was also noticed that the performance of this specimen deteriorated with each subsequent experiment. This was later found to be due to a gradual transformation of white tin to the grey form. On account of these difficulties, experiments with the laminated specimen were abandoned and it was decided to reduce the eddy current heating by alloying the specimen; this increases the resistivity of the metal and also prevents superheating. In choosing the impurity for tin, the following considerations were important:

- (1) The impurity should form a solution in tin so that the alloy is as strain-free as possible. This was necessary to prevent local regions of very high critical fields due to the so-called 'Mendelssohn sponge';¹² and
- (2) The thermodynamic properties of tin should not be altered drastically by the impurity.

Indium, which has the same order of atomic diameter as tin, is known to form a substitutional solution with tin in concentrations up to 3 per cent. Doidge¹³ has shown that the difference in thermodynamic properties of tin and tin-indium alloys up to 3 per cent is very small. Transition temperatures are only slightly lower than that of tin and the critical field curves indicate that the electronic specific heat remains virtually unchanged.

In order to study the effect of alloying, three specimens containing 0.5, 1, and 2 per cent indium were prepared. Their sizes and shapes were the same as the original cylinder of pure tin. The use of alloys with a higher concentration of indium was not contemplated because of the evidence¹³ that the interphase energy becomes negative at about 2.5 per cent of indium. According to H. London,¹⁴ a negative interphase energy can cause thin superconducting filaments to persist in fields greater than the critical, and it was feared that these might cause a reduced drop in temperature on magnetization. All the three specimens were annealed at a temperature of 200°C for 3 weeks before magnetization. The lowest temperatures obtained are shown in Table 2.

Table 2

Indium concentration (per cent (wt))	Final temperature (°K)
0.5	0.192
1.0	0.180
2.0	0.345

The temperatures 0.192°K and 0.180°K, although substantially lower than 0.35°K attained with pure tin, are still a good deal higher than the expected value of 0.02°K. These specimens were magnetized by using d.c. mains as a source of excitation for the electromagnet, and this may have possibly resulted in an excessive heating during the magnetization. The final temperature of 0.345°K obtained with the 2 per cent specimen was due to the Mendelssohn sponge behaviour. This was evident from the fact that on increasing the field beyond 305 oersteds the specimen showed slight further cooling in small steps. This, however, could not be utilized for obtaining a lower temperature because in raising the field the specimen warmed up as a whole.

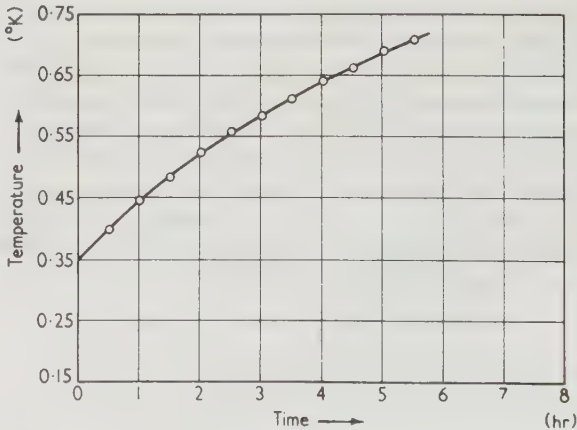


Figure 5. Diagram of rise in temperature versus time curve for pure tin in a steady field

Warming-up rates

In order to assess quantitatively the value of the method, it was necessary to measure the rate at which the specimens warm up after magnetization. Figure 5, which is a plot of the rise in temperature against time for pure tin in a steady (battery) field of 305 oersteds, shows that it takes more than 6 hr to reach 0.75°K. This compares favourably with the warming-up rates of an average demagnetization cryostat in the same range. The alloys which were magnetized in the fluctuating mains field showed a much faster rate of warming, as can be seen from Figure 6. On a more careful examination of the curves in Figure 6, we find that the

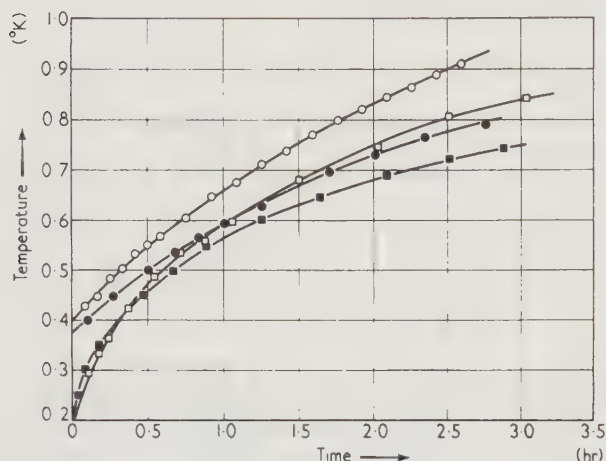


Figure 6. Diagram of temperature versus time curves for pure tin and tin-indium alloys

1 per cent alloy has the fastest average rate of rise in temperature and the 0.5 per cent the slowest. This seems surprising because, if the increase in the rate of warming-up is caused by Joule heating in the normal metal the 2 per cent alloy should have the slowest rate and the 0.5 per cent the fastest, since Joule heating is inversely proportional to the resistivity of the metal. The frequency of the ripple and the resistivities of our alloys were such that skin depth considerations were unimportant. Another feature of these curves is that the 0.5 per cent alloy, although it warms up more slowly on the average, between 0.2 and 0.4°K its rate of rise in temperature is greater than that for the 1 per cent alloy, which warms up at a higher rate on the whole. At 0.4°K, a temperature which is common to all the three specimens, the slopes of these curves are approximately in the following ratios:

$$0.5\%:1\%:2\% = 1:1.3:0.8$$

whereas at 0.6°K they change over to

$$0.5\%:1\%:2\% = 1.4:0.8:1.0$$

This behaviour could be explained either by assuming that the resistivities of these alloys were changing with

temperature, or by a change of specific heats, or by both. The likelihood of a change in specific heat was rather small, since a fairly rapid change would have to be assumed to explain the result. On the other hand, a change of effective resistance with temperature in the presence of a magnetic field is possible. The fields required to restore completely the resistance in an alloy are much higher than the fields necessary for the flux to penetrate. This means that a very small fraction of the total volume of the alloy remains superconducting and has a higher critical field curve. Thus, it is possible that because of field fluctuations a portion of the material at a particular temperature alternates between the normal and the superconducting phase, causing a good deal of irreversible heating. The rate of warming-up at a particular temperature in alloys would depend on the amount of material which alternates between the two phases and on the residual resistance of this material. On warming-up, more and more of this material becomes permanently normal, until a temperature is reached where the transition to the normal state is complete and the warming-up becomes steady. Beyond this point the heating rate will depend only on the resistivity of the alloy.

This explanation is supported by a more detailed investigation of the warming-up curves over a wider temperature range. In the 0.5 and 1 per cent alloys it was noticed that the rate of warming-up showed discontinuous changes. Assuming that this was due to a sudden change in heat input and not to a discontinuous change in specific heat, the curves shown in Figure 7 were plotted. Here, the specific heat for all three specimens was supposed to be

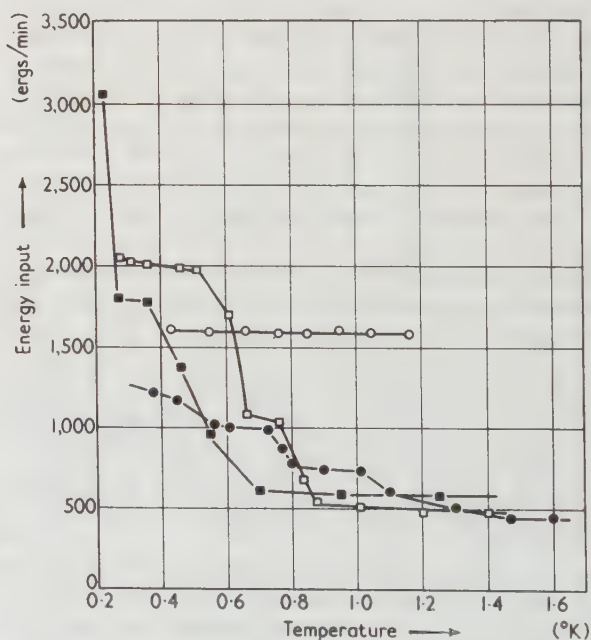


Figure 7. Diagram of energy input versus temperature curves for pure tin and tin-indium alloys

the same as for pure tin. Using the empirical values of Corak and Satterthwaite,¹⁵ the energy input per minute was calculated from the observations and plotted against temperature. All the three curves show marked discontinuities, which can be explained by assuming that at certain temperatures a small but finite amount of material goes over to the normal state permanently and causes a corresponding decrease in irreversible heating. This goes on until the whole of the alloy is normal. The curves then cease to show these discontinuities and attain a steady value. For the 0.5 per cent alloy this seems to occur at 0.7°K and for the 1 per cent alloy at about 0.88°K. The 2 per cent alloy, which is likely to have greater inhomogeneities, does not seem to lose all its superconducting material until about 1.5°K. Above this temperature, where all the specimens show a steady heat input, we find that the lowest value is for the 2 per cent alloy and the highest for the 0.5 per cent alloy. This seems eminently reasonable, because their electrical conductivities are also in the same sequence.

In spite of the excessive heating caused by the ripple field, the rate of temperature rise in our specimens was slow enough to allow quantitative measurements below 1°K. This was proved in subsequent experiments by making measurements of specific heats of our specimens down to 0.5°K. Moreover, the mechanism suggested here is further supported by our measurements of the specific heat (to be reported elsewhere).

Low temperature thermometry and its accuracy

The errors involved in measuring the low temperatures achieved depended mainly on the sensitivity of the magnetic thermometer used for calibrating the resistors. It consisted of a conventional type of mutual inductance bridge using an external compensating coil. On switching off a current of 100 mA in the primary circuit of this bridge, a galvanometer deflection of 365 mm was obtained at 1°K on a scale which was 4 m distant. The galvanometer deflection for all measurements below 1°K was kept roughly at 400 mm and a $\tan \delta$ correction of 0.5 per cent was applied. The slope of the deflection against $1/(T - \Delta)$ line, where Δ is the Curie-Weiss constant, was calculated by the method of least squares and gave a value of 364.4 ± 0.9 , which was used for calculating the temperature below the helium range. Since the galvanometer deflection could be measured to about one part in 1,500, the errors in the

temperatures were governed by the probable error in the slope quoted above. A larger probable error than the accuracy of measurement was caused by the fact that above 1°K the actual deflections were much less than 400 mm and, consequently, the accuracy was not so great. Resistance measurements could be made to at least an accuracy of one in 4,000 and, therefore, the actual temperatures quoted are again accurate to the order obtained by the magnetic thermometer. We must not forget, however, that below 0.5°K the chief error in the values of absolute temperature is due to the errors in the $T-T^*$ relation which are at least of the order of 2 per cent.

The author wishes to express his thanks to Dr. K. Mendelssohn, F.R.S., for suggesting the problem and for his help and encouragement. He is also grateful to the Tin Research Institute, London, for supplying the vast quantities of pure tin used in the experiments. A part of this work was done during the tenure of Twisden Studentship in Experimental Physics, awarded by Trinity College, Cambridge.

REFERENCES

1. KEESOM, W. H., and KOK, J. A. *Proc. Acad. Sci. Amst.* **35**, 743 (1932)
2. MENDELSSOHN, K., and MOORE, J. R. *Nature, Lond.* **133**, 413 (1934)
3. KEESOM, W. H., and KOK, J. A. *Physica* **1**, 595 (1934)
4. DAUNT, J. G., MENDELSSOHN, K., and PONTIUS, R. B. *Actes, VII^e Congrès International de Froid* **1**, 445 (1936)
5. DAUNT, J. G., and MENDELSSOHN, K. *Proc. roy. Soc.* **A160**, 127 (1937); DAUNT, J. G., HORSEMAN, A., and MENDELSSOHN, K. *Phil. Mag.* **27**, 754 (1939)
6. DAUNT, J. G., and MENDELSSOHN, K. *Proc. roy. Soc.* **A185**, 225 (1960)
7. CORAK, W. S., GOODMAN, B. B., SATTERTHWAITE, C. B., and WEXLER, A. *Phys. Rev.* **96**, 1442 (1954)
8. GOODMAN, B. B. *Conférence de Physique des Basses Températures, Paris*, p. 506 (I.I.F., Paris)
9. BARDEEN, J., COOPER, L. N., and SCHRIEFFER, J. R. *Phys. Rev.* **108**, 1175 (1957)
10. MENDELSSOHN, K., and RENTON, C. A. *Phil. Mag.* **44**, 776 (1953)
11. GARRETT, C. G. B. *Phil. Mag.* **41**, 621 (1950)
12. MENDELSSOHN, K. *Proc. roy. Soc.* **A152**, 34 (1935)
13. DOIDGE, P. R. *Phil. Trans.* **248**, 553 (1955)
14. LONDON, H. *Proc. roy. Soc.* **A152**, 650 (1935)
15. CORAK, W. S., and SATTERTHWAITE, C. B. *Phys. Rev.* **102**, 662 (1956)

M. Yaqub is now at Washington University, St. Louis, Missouri, U.S.A.

Superfluidity and Specific Heat of Liquid Helium in 'Vycor' Porous Glass

D. F. Brewer, D. C. Champeney, and K. Mendelssohn

Clarendon Laboratory, Oxford

Received 19 September 1960

EXPERIMENTS on unsaturated helium films have shown that phenomena associated with superfluidity in liquid helium are depressed to lower temperatures when the thickness is reduced below that of the saturated film ($\sim 10^{-8}$ cm). For instance, the work of Bowers, Brewer, and Mendelssohn^{1,2} and of Long and Meyer^{3,4} demonstrated that the temperature of onset of superflow is lower in such thin films than the normal lambda temperature. Frederikse^{5,6} and Aston and Mastrangelo⁷ showed that the temperature of the specific heat maximum also decreases with film thickness. Comparison of these two types of experiment reveals an unexpected feature, namely that the specific heat maxima are consistently higher than the onset temperatures for superflow by about 0.4° K, while in the bulk liquid both of the temperatures are the same within the experimental accuracy.

A natural extension of these experiments is the investigation of 'bulk' liquid helium confined in channels of dimensions similar to those of the unsaturated film. 'Vycor' porous glass, described by Nordberg⁸ provides a suitable material for such experiments, having a sponge-like structure permeated by pores whose mean diameter depends upon the sample used, and varies between about 30 and 100 Å. Atkins, Condon, and Seki⁹ showed that the temperature of onset of superflow through specimens of this glass was indeed depressed below the ordinary lambda point.

In some respects, experiments using 'Vycor' are more difficult to interpret than those on unsaturated films, since the pore size distribution is not known accurately, and the analysis of results is thus complicated. On the other hand, when comparing different aspects of the lambda transition with one another, 'Vycor' provides the advantage that for both types of experiment the pore size is the same, so that flow and specific heat measurements can be compared with a good degree of reliability, whereas with unsaturated films, the phenomena must be correlated with film thickness through the adsorption isotherms, which have been found to give inconsistent results.^{10,11} With this situation in mind, we have measured the flow properties and specific heat of liquid helium in 'Vycor' glass as a function of temperature using the same sample for both sets of experiments. The pore diameter has been measured in the course of a separate investigation of adsorption, again in the same specimens, by Brewer and Champeney.¹² A brief

report of some of the results in the present paper has appeared elsewhere.¹³

Flow experiments

Experiments were carried out to determine the rate of flow at a given pressure head as a function of temperature for several specimens of 'Vycor' glass. From these measurements, the temperatures of onset of superflow were determined, and suitable specimens chosen for use in specific heat measurements. The principle of the method was that generally used for isothermal gravitational flow experiments on liquid helium. A glass reservoir was first filled by total immersion in a bath of liquid helium, then partially lifted out and the level within it measured as a function of time while liquid flowed out through a disk of 'Vycor' sealed to the bottom of the vessel. The flow rate at a given pressure head was determined from the graph, and the experiment repeated at different temperatures.

A typical form of the reservoir is shown in Figure 1. The side tube was a capillary of 1 mm bore which provided

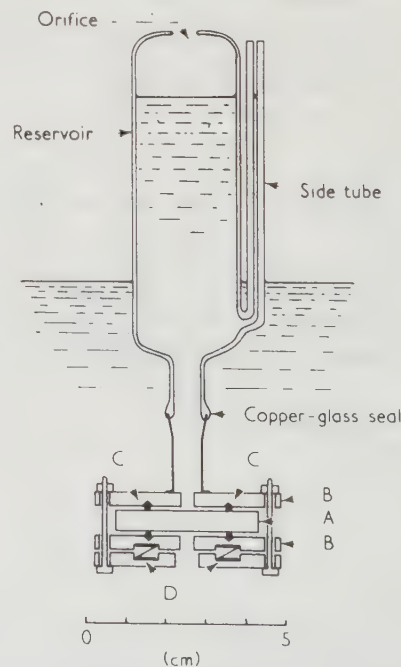


Figure 1. The flow apparatus showing 'Vycor' disk and clamp

a clear meniscus for viewing. A similar tube was fixed beside it, open at both ends and dipping into the bath, for observing the bath level and compensating for capillary rise in the side tube. A scale engraved in half millimetres was supported just behind these tubes, and the levels estimated to a tenth of a millimetre by observation through the glass Dewar system using a long focus microscope.

The 'Vycor' disk, of thickness 5 mm and diameter 3.6 cm, was sealed to the reservoir using a system involving indium gaskets. The disk (A) was sandwiched between two brass plates (B), with indium gaskets (C) 1.5 mm thick above and below, fitting into grooves in the brass. The assembly was tightened by means of six bolts around the rim with spring washers (D), and was connected to the glass reservoir with a copper-to-glass seal.

The area of the disk accessible to flow was limited by the diameter of the upper gasket, the lower one acting solely as a cushion to prevent the disk from cracking. Two sizes of gasket could be used having nominal diameters, before compression, of 2 cm and 0.5 cm. Under pressure they flattened out, and the actual diameter effective in describing the area for liquid flow was different from the nominal diameter.

Experiments were performed with three reservoirs of different dimensions so that a large range of flow rates could be observed without the rate of fall of meniscus becoming too quick to measure. The gasket diameter d_g , reservoir diameter d_r , and reservoir orifice diameter d_o for the three flow vessels are given in Table 1. The gasket diameters refer to the measured internal diameters after compression. The orifice diameter is included because of its importance in the effective action of the distillation process discussed below, which maintains the reservoir

and bath at similar temperatures. Flow vessels I, II, and III were used, respectively, in the temperature ranges 1.22 to 1.97° K, 1.84 to 2.05° K, and 2.04 to 2.11° K, and the results obtained were pieced together to give information over the whole range.

Other 'Vycor' specimens were available in the form of 'thimbles' or short test-tubes. For these, a simpler form of apparatus was used, consisting of a glass reservoir of suitable diameter, constricted at the top to limit film flow, and attached to the 'Vycor' by a graded seal.

Table 1

Flow vessel	d_g (cm)	d_r (cm)	d_o (cm)
I	0.35	2.5	0.5
II	1.74	2.5	0.5
III	1.74	0.35	0.11

In Figure 2 we show typical graphs of the rate of change of reservoir and bath levels as a function of time at three temperatures for one of the 'Vycor' disks. Similar curves were found for other specimens, and from such graphs as these the net rate of outflow at a given pressure head was determined by drawing tangents to the 'reservoir' curves. In the case of flow vessel I the flow rate was then expressed as cubic centimetres per minute per square centimetre of 'Vycor', using the known values of d_r and d_g . Results

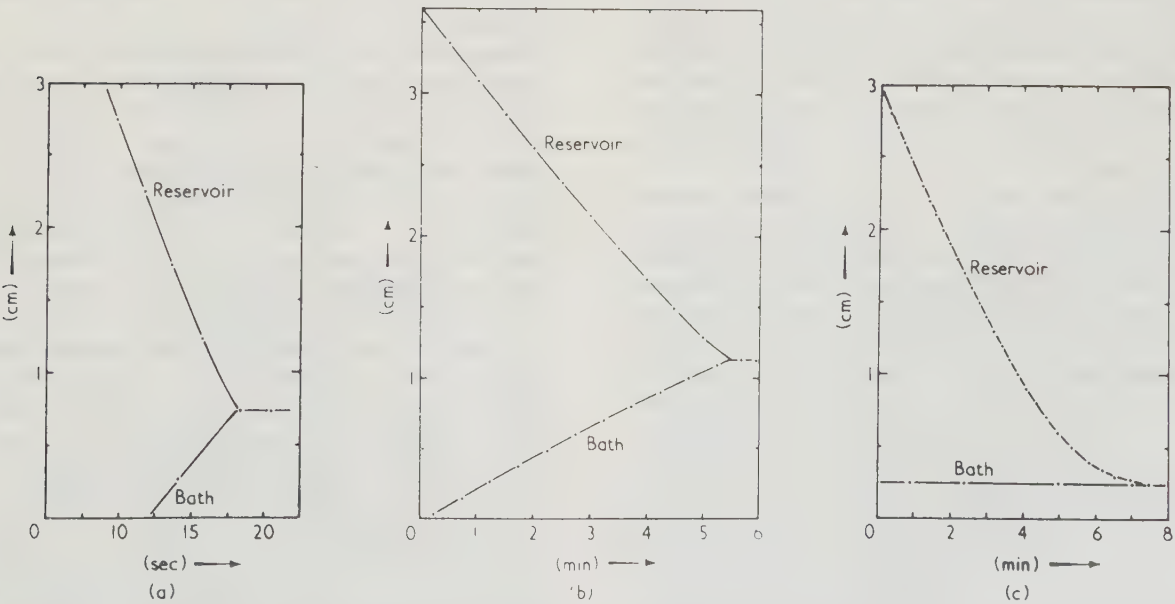


Figure 2. Variation of liquid levels in reservoir and bath with time for different reservoirs and temperatures; (a) $T = 1.22^{\circ}\text{K}$, reservoir I; (b) $T = 1.911^{\circ}\text{K}$, reservoir II; (c) $T = 2.05^{\circ}\text{K}$, reservoir III

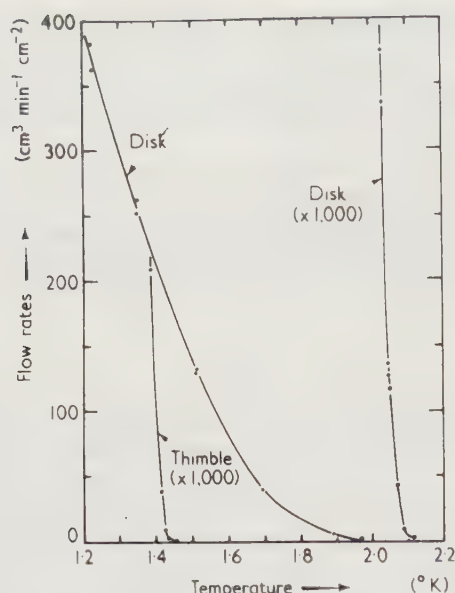


Figure 3(a). Flow rate F versus temperature for constant level difference of 2 cm

similarly calculated using flow vessel II consistently differed from those obtained with vessel I at the same temperature, being four times smaller. It is reasonable to assume that this is due to the differing geometries of flow path as in neither case would the flow have been uniformly perpendicular to the plane of the disk. Results with flow vessels II and III were therefore scaled by the same factor to join on to those with vessel I. This uncertainty in the absolute flow rate per unit area of 'Vycor' should not, however, affect its general temperature variation.

Appreciable corrections had to be made to the flow rates thus determined, due to film flow and to evaporation from the reservoir. The effect of film flow was estimated from the orifice diameter and the values of film transport over clean glass surfaces given by Daunt and Mendelssohn.¹⁴ In vessel III this correction amounted to 20 per cent at 2.11° K, falling to 1 per cent at 2.05° K. Otherwise it was negligible.

Excess evaporation from the reservoir occurs as a result of the mechano-caloric effect¹⁵ when superfluid flows out through the 'Vycor' disk, and through the film. It was allowed for by dividing the observed rate of fall of level by $(1 + ST/L)$ where S and L are the specific entropy and latent heat of helium at the temperature T . This expression is based on the assumptions that no entropy is carried out of the reservoir by the liquid helium flowing through the 'Vycor' and the film, and that the effective mechano-caloric heat input is entirely removed by the distillation process discussed in detail by Atkins.¹⁶ The first of these assumptions is contained in London's equation¹⁷ for the thermomechanical effect, which has been tested frequently and verified for even larger channels than those involved here. The effectiveness of the distillation process was tested separately for each reservoir by performing repeated

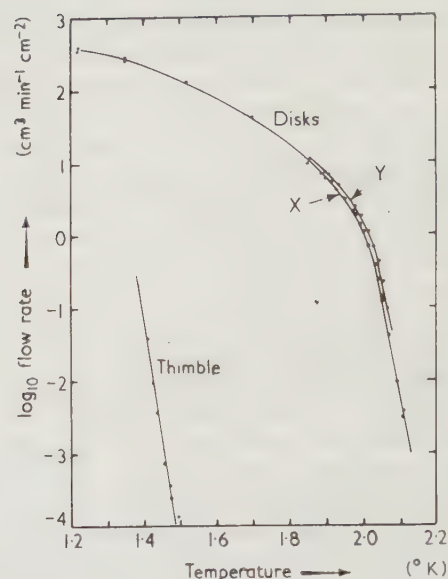


Figure 3(b). $\log F$ versus temperature for constant level difference of 2 cm

flow experiments at the same bath temperature, but with various currents applied to an electric heater inside the reservoir. Heat inputs of up to 1.5 times the effective mechano-caloric heat input were applied and were found to result simply in an increased rate of fall of meniscus equal to that calculated as resulting from an increased rate of evaporation. This fact was taken as satisfactory evidence that the flow rate through the 'Vycor' was not affected by any small temperature differences between reservoir and bath, and also that any heat produced in the reservoir was removed by distillation rather than by conduction through the glass. Tests of this nature were performed throughout the temperature ranges used with each vessel.

In order to plot the flow rate through a given 'Vycor' specimen as a function of temperature, it is necessary to choose a standard pressure head for all temperatures, since, as the graphs of Figure 2 show, the flow is strongly pressure dependent. Choosing a pressure head of 2 cm, we obtain curves of flow rate F versus temperature as shown in Figure 3(a) for two specimens, in which the corrections described above have been included. Curves of similar shape are obtained for other pressure heads, but with different magnitudes of the flow rate. Onset temperatures for superflow may conveniently be obtained from the logarithmic plots of Figure 3(b) by a method explained in the final section. Qualitatively, it may be seen from Figure 3(a) that onset temperatures between about 1.4° K and 2.1° K are found in the specimens investigated. The lower onset temperatures were, however, obtained with the 'thimble' specimens which were not suitable for specific heat and adsorption measurements. For the latter experiments, the two disks giving curves labelled X and Y in Figure 3(b) were finally chosen, having onset temperatures very close to each other.

Specific heat experiments

The heat capacity of helium contained in the pores of the 'Vycor' disks under saturation conditions was measured by the usual method, employing an adiabatic vacuum calorimeter. The results were calculated from the temperature increases produced by known electrical heat inputs. The apparatus is shown in Figure 4.

The disks fitted, with little dead space, into a copper calorimeter which was suspended inside a vacuum jacket. The outside of the jacket was maintained at 4.2°K . The calorimeter had attached to it an auxiliary container into which a small quantity of liquid helium could be condensed. By pumping on this helium, the calorimeter could be cooled to 1.2°K ; measurements were begun after this liquid had completely evaporated.

The calorimeter was filled with helium gas from a storage vessel of known volume and the amount of liquid helium in the calorimeter was calculated from the decrease in pressure of this vessel. Corrections were applied for the amount of gas filling the dead space in the inlet tubes. The same apparatus was used for measuring adsorption isotherms of helium and nitrogen on these specimens of 'Vycor', and the volumetric system and method of allowing for dead space corrections will be described more fully along with that work.¹²

To reduce heat inputs the inlet tubes were coiled in passing from the vacuum jacket to calorimeter, and consisted of 30 cm of 1 mm diameter german silver tubing. The heat leak into the calorimeter was chiefly due to film flow along these tubes and amounted to $1.4 \times 10^{-4}\text{ W}$ at 1.4°K , falling to a steady value of $8 \times 10^{-6}\text{ W}$ above 2.18°K .

The temperature of the calorimeter was measured with a carbon resistance thermometer calibrated against the

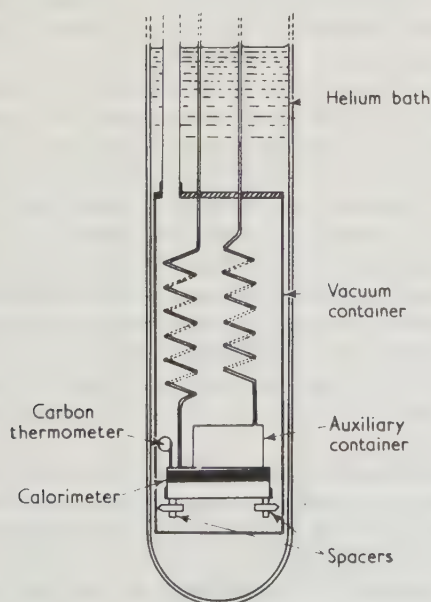


Figure 4. Specific heat apparatus

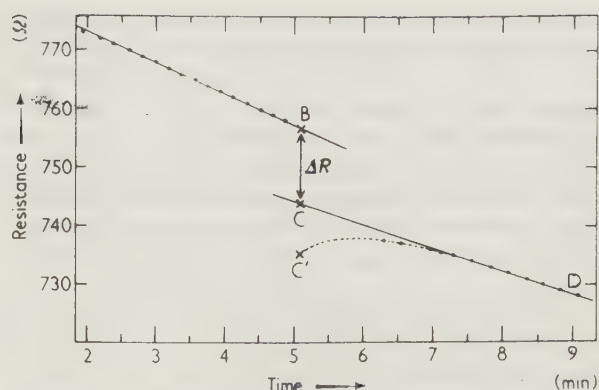


Figure 5. Change in resistance thermometer versus time during a typical warm-up period

vapour pressure of helium within the calorimeter, using the T_{55} experimental temperature scale and correcting for thermo-molecular effects at the lower temperatures as described by Keesom.¹⁸ Changes in conductance of the thermometer with temperature, $d(1/R)/dT$, were measured to an estimated accuracy of 1 per cent. The heater consisted of approximately $450\ \Omega$ of 40 s.w.g. constantan wire wound on to the body of the calorimeter, arranged with potentiometer leads so that its resistance could be accurately determined.

The heat capacity C of the system was calculated from the relation

$$C = \frac{i^2 r t}{\Delta(1/R)} \frac{d(1/R)}{dT}$$

where $\Delta(1/R)$ was the change in conductance of the thermometer resulting from the passage of a current i for time t through the heater of resistance r . In determining the true specific heat of the liquid helium within the 'Vycor' pores, the following factors and corrections have been considered: (1) the effect of non-equilibrium within the calorimeter and the variation of warm-up rate with temperature; (2) the heat capacities of any excess liquid present, of the metal calorimeter, and of the 'Vycor' glass; (3) the heat taken up in evaporation during warming.

With regard to the first, a typical portion of warm-up curve is shown in Figure 5. In the diagram, the resistance change ΔR is obtained by a straight line extrapolation along DC, C being in the centre of the 30 sec heating period. However, a straight line extrapolation was not permissible since the rate of warm-up changed rapidly with temperature due to the rapidly varying heat capacity and the variation in heat leak through the film. Allowance had also to be made for the time taken for temperature equilibrium to be attained within the calorimeter, the initial non-equilibrium being indicated by the curved portion C'D. These effects meant that values obtained using the simple straight line extrapolation had to be corrected by an amount varying from 20 per cent at 1.5°K to less than 1 per cent above 2.1°K .

The calorimeter contained a small amount of free liquid in excess of that inside the 'Vycor' pores. By following the

adsorption isotherm during filling, this free liquid could be measured accurately, and amounted to 1.70×10^{-3} g and 4.80×10^{-3} g in two experiments, as compared with 0.48 g contained in the 'Vycor'.

The copper calorimeter weighed 53 g, and the 'Vycor' disks when dry weighed together 14.77 g. The heat capacities were estimated from the specific heats of copper and 'Pyrex' given by Wolcott.¹⁹ These amounted together to a 1 per cent correction at 2.3° K and less at lower temperatures.

As the calorimeter temperature T rose and the vapour pressure P increased, liquid helium evaporated, thus increasing the mass of helium gas m , in the dead space in the inlet tube. A quantity dQ/dT was subtracted from the apparent heat capacity, using the relation

$$\frac{dQ}{dT} = L \frac{dm}{dP} \frac{dP}{dT}$$

In this equation L was taken as the latent heat of bulk liquid helium. In a subsidiary experiment in which the 'Vycor' disks were replaced by solid copper disks of the same size, m was measured as a function of pressure at various temperatures enabling dm/dP to be deduced. This correction amounted to 10 per cent at 2.3° K falling to 1 per cent at 1.6° K.

The final results for the specific heat of the helium within the 'Vycor', after application of the corrections, are given in Figure 6.

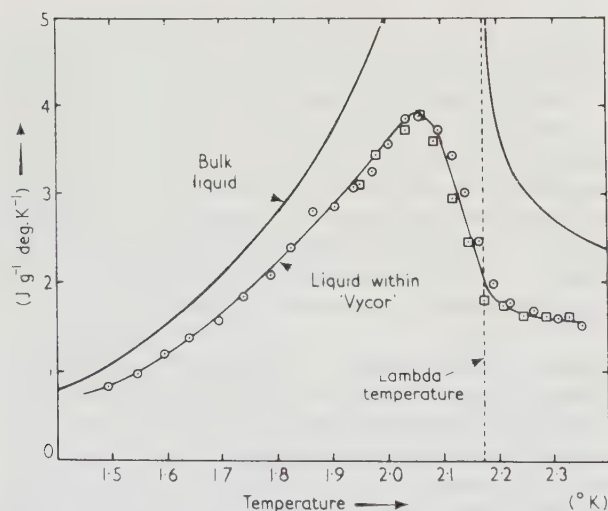


Figure 6. Specific heat versus temperature of liquid helium-4 contained within 'Vycor' porous glass. Circles and squares refer to different experiments

Discussion

It is apparent from Figure 3(a) that the graph of flow rate F versus temperature is convex towards the origin, as distinct from those in somewhat wider channels or with the saturated helium-II film where it is concave. The question naturally arises as to where such a curve ultimately reaches

the abscissa, if at all. The situation is complicated by the effects of the pore size distribution, which presumably result in a small amount of flow right up to the lambda point of bulk liquid. As a simple criterion we shall assume that the region over which $(1/F)(dF/dT)$ assumes its maximum value represents the onset temperature. If the curve actually met the temperature axis this function would be infinite. The graph in Figure 3(b) shows that $d(\log F)/dT$ reaches a maximum value between 2.0 and 2.1° K for specimens X and Y and we shall assume that the onset temperature for the predominant pore size occurs within this interval. The straight portion of the curve, relating to onset of superflow, was found to be similar for different samples having onset temperatures down to 1.4° K, being simply shifted parallel to the temperature axis with little change of slope.

With regard to the convexity towards the origin of our flow rate versus temperature curve, it is worth noting that the curves obtained by Brewer and Mendelssohn^{2,20} for the flow of unsaturated films were of very similar shape except that at temperatures within 0.1° K of the onset temperature they straightened out and intercepted the temperature axis at a finite angle.

This onset temperature for superflow may be compared with the temperature 2.06° K at which the specific heat curve shows a maximum, and it appears that the two temperatures are identical within about 0.1° K. On the other hand, Long and Meyer¹¹ have drawn attention to an apparent difference of about 0.4° K between the specific heat maximum and the onset temperature of unsaturated films. However, in arriving at this figure they found it necessary to analyse the results of different authors using different adsorbents, and to compare readings at the same value of P/P_0 ^{10,11}. Adsorption isotherms measured by different authors vary considerably even on the same material, so the actual thicknesses of film at the chosen value of P/P_0 might have been considerably different. The present comparison is free from this difficulty.

Another point of interest lies in the relationship between pore diameter and onset temperature of superfluidity. Atkins et al.⁹ have reported results for several specimens of 'Vycor' and these are listed below along with our values in Table 2. In order to compare these results with ours it is necessary to ascertain that the same criterion for choosing the onset temperature has been used in both cases. Atkins et al. chose the onset temperature as that at which the liquid level moved at about 0.01 cm sec⁻¹ and using rough figures for the dimensions of their apparatus this corresponds to about 0.01 cm³ min⁻¹ per cm². Reference to Figure 3(b) shows that this is approximately the same criterion as chosen by us.

It would be of interest next to compare the 'Vycor' pore diameter appropriate to a certain onset temperature with the thickness of an unsaturated film of the same onset temperature. This, however, can only be done approximately because of the uncertainty of film thickness in the experiments on unsaturated films. In the fourth column of Table 2 we give the percentage of saturation pressure

Table 2. Onset Temperatures in 'Vycor' and in Unsaturated Films

Author	Onset temperature (°K)	Average pore diameter (Å)	P/P ₀ (per cent)	Film thickness (Strauss) (Å)	Film thickness (Frederikse) (Å)
Atkins et al.	1.36	42	48	11	16.5
Atkins et al.	1.64	50	79	17	28
Atkins et al.	1.68	57	82	18.5	31
Atkins et al.	1.78	57	88	23.5	—
Present work	2.0-2.1	70	96-98	—	—

necessary to yield the same onset temperature as the 'Vycor'. These figures were obtained by smoothing the results obtained by Brewer and Mendelssohn² and by Long and Meyer.⁴ The fifth and sixth columns list the corresponding unsaturated film thicknesses, calculated using respectively the isotherms of Strauss¹¹ and of Frederikse and Gorter.²¹ Of the several different isotherms published, these two represent extreme values. We have calculated the thicknesses on the assumption that the film consists of a helium substrate 4.8 Å thick and of density 0.21 g cm⁻³, and that this is covered by adsorbate of liquid density.¹² Unfortunately, the isotherms do not extend to high enough pressures for a comparison with the present data.

It thus appears that the film thickness at which, at a given temperature, superfluidity sets in is considerably less than the corresponding average pore diameter. If the porous structure consisted of large cavities connected by narrow constrictions, then it is possible that the actual diameter determining the flow in the 'Vycor' would be less than the mean pore diameter. However, the specific heat is a bulk property not affected appreciably by constrictions, and if the structure were as indicated above one would

expect the onset temperature of superflow to be below that of the specific heat maximum. Our results thus favour the alternative suggestion that depression of the lambda transition is caused by the forces of attraction to the wall. Since in 'Vycor' glass the liquid is completely surrounded by solid walls, the effect of attractive forces is greater than in the film, where the forces operate on only one side.

We are grateful to Dr. M. E. Nordberg of the Corning Glass Research Laboratories for supplying us with the glass samples used in this research.

REFERENCES

1. BOWERS, R., BREWER, D. F., and MENDELSSOHN, K. *Phil. Mag.* **42**, 1445 (1951)
2. BREWER, D. F., and MENDELSSOHN, K. *Proc. roy. Soc.* In print.
3. LONG, E. A., and MEYER, L. *Phys. Rev.* **85**, 1030 (1952)
4. LONG, E. A., and MEYER, L. *Phys. Rev.* **98**, 166 (1955)
5. FREDERIKSE, H. P. R. *Physica* **15**, 860 (1949)
6. FREDERIKSE, H. P. R. *Thesis* (Leiden, 1950)
7. ASTON, J. G., and MASTRANGELO, S. V. R. *J. chem. Phys.* **19**, 1370 (1951)
8. NORDBERG, M. E. *J. Amer. ceram. Soc.* **27**, 299 (1944)
9. ATKINS, K. R., SEKI, H., and CONDON, E. U. *Phys. Rev.* **102**, 582 (1956)
10. BREWER, D. F., and MENDELSSOHN, K. *Phil. Mag.* **44**, 789 (1953)
11. LONG, E. A., and MEYER, L. *Advanc. Phys.* **2**, 1 (1953)
12. BREWER, D. F., and CHAMPENEY, D. C. To be published
13. CHAMPENEY, D. C. *Low Temperature Physics and Chemistry*, p. 27 (University of Wisconsin Press, Madison, 1958)
14. DAUNT, J. G., and MENDELSSOHN, K. *Proc. roy. Soc.* **A170**, 423, 439 (1939)
15. DAUNT, J. G., and MENDELSSOHN, K. *Nature, Lond.* **143**, 719 (1939)
16. ATKINS, K. R. *Proc. phys. Soc. Lond.* **A64**, 833 (1951)
17. LONDON, H. *Proc. roy. Soc.* **A171**, 484 (1939)
18. KEESOM, W. H. *Helium* (Elsevier, Amsterdam, 1942)
19. WOLCOTT, N. M. *Thesis* (Oxford, 1956)
20. BREWER, D. F. *Thesis* (Oxford, 1953)
21. FREDERIKSE, H. P. R., and GORTER, C. J. *Physica* **16**, 402 (1950)

Discussion on Enthalpies of Mixtures

M. Ruhemann Petrocarbon Developments Ltd, Manchester

Received 17 August 1960

COMMISSION I of the International Institute of Refrigeration, meeting at Eindhoven at the end of June, devoted a special session under the chairmanship of the author to 'Enthalpy Ignorance', the lack of information on the enthalpies of gaseous and liquid mixtures. Short contributions were made by invited speakers followed by a general discussion of the subject.

In an introductory statement, Dr. P. J. Haringhuizen (Staatsmijnen, Limburg) pointed out that the design of low temperature gas separation plants requires a knowledge of the enthalpies of gaseous mixtures as a function of pressure, temperature, and composition. Whereas fairly reliable charts and tables exist for the thermodynamic properties of most of the components occurring in these mixtures, the properties of the mixtures themselves are little known.

At low pressures and well above the critical temperatures of all the components, the enthalpy may, as a first approximation, be taken as a linear combination of the enthalpies of the constituents, neglecting the heat of mixing. However, at high pressures and low temperatures, this is certainly not permissible. As an example, Dr. Haringhuizen showed a plot of the enthalpy of a 3:1 hydrogen-nitrogen mixture as a function of pressure up to 400 atm for several temperatures above 0°C, which had been established experimentally by Michels and colleagues at Amsterdam. On the same plot calculated enthalpies were shown, using a linear combination of the component enthalpies based on the total pressure and, alternatively, on the partial pressures of the components in the mixture. Both theoretical curves showed marked deviations from the experimental values, the curves based on the total pressure being 'worse' than those using partial pressures, and the deviations became greater the lower the temperature.

An additional difficulty arises when, as is frequently the case at the required temperatures and pressures, one or several of the pure components exist by themselves in the liquid state only. It is evidently incorrect to insert the enthalpies of the pure liquids in the linear combinations intended to give the enthalpies of the gaseous mixtures.

Proposals have been made to calculate enthalpies of hydrocarbon mixtures on the assumption that they depend only on the molal average boiling point, but these methods are largely empirical and have no sound thermodynamic basis.

In addition to the enthalpies of gas mixtures, those of the corresponding liquids are also required for design purposes, and our knowledge of the heats of mixing of liquids is still very fragmentary. Moreover, little or no information is available to assess the heat to be withdrawn from a mixture under conditions of partial condensation in the presence of non-condensing components.

Dr. Z. Dokoupil (Kamerlingh Onnes Laboratory, Leiden) gave an example of how the enthalpy of a gas mixture can in principle be evaluated on the basis of P - V - T data for the individual components with the help of a suitable equation of state. Taking the $3\text{H}_2 + \text{N}_2$ mixture treated by Dr. Haringhuizen, for which experimental data are available, and using the Beattie-Bridgeman equation of state, the relevant constants of which have been tabulated for the pure components, he calculated the constants for the mixture with the conventional combination rules. He then computed the enthalpy of the mixture along the 100°C isothermal, using well known thermodynamic relationships, and found that the results hardly deviated from the curve based on the experimental P - V - T data up to 400 atm pressure. If the constants of the Beattie-Bridgeman equation are adjusted to fit the experimental data for the pure components as accurately as possible in the field of temperature and pressure covered, still better agreement can be obtained for the mixture.

It may be inferred that this method is applicable to certain gas mixtures at relatively high temperatures up to pressures of several hundred atmospheres, but it may well become inaccurate at low temperatures and cannot be used below the critical temperatures of any of the components.

Dr. F. Din (British Oxygen Research and Development Ltd., London) approached the problem from the opposite side by demonstrating a method of calculating the heat of mixing of liquid oxygen and nitrogen at low pressure from liquid-vapour equilibrium data. This system had been investigated experimentally by the author over the complete range of compositions and an adequate field of temperature and pressure. The results enabled the expression $\ln(\gamma_1/\gamma_2)$ to be calculated from the relative volatility and the fugacities of liquid and vapour, where γ_1 and γ_2 are the activity coefficients of nitrogen and oxygen. It will be recalled that the activity coefficient may be defined by

$f_i = f_i' \gamma_i x_i$, where f_i is the fugacity of component i in the solution, f_i' the fugacity of the pure component at the same temperature and at the total pressure of the solution, and x_i is the mole fraction.

Now the excess free energy $\Delta G^{(E)}$ (free energy of real solution minus free energy of ideal solution) can be evaluated from the equation

$$\left(\frac{\partial \Delta G^{(E)}}{\partial x_i} \right)_T = RT \ln \left(\frac{\gamma_1}{\gamma_2} \right)$$

and this was done for temperatures of 80 and 90° K.

The required heat of mixing is in fact the excess enthalpy $\Delta H^{(E)}$ of the mixture since the enthalpy of mixing of the ideal solution is zero.

Unfortunately, the corresponding integral equation involving the excess enthalpy of mixing $\Delta H^{(E)}$ does not allow the latter to be evaluated unless it is a very simple function of composition, e.g. of the form Ax_1x_2 , where A is a constant. Values obtained with the Gibbs-Helmholtz equation are not sufficiently accurate. It may, however, be tentatively assumed that liquid mixtures of oxygen and nitrogen behave as 'regular' solutions for which, by definition, the excess entropy of mixing $\Delta S^{(E)} = 0$. In this case, since

$$\Delta G^{(E)} = \Delta H^{(E)} - T\Delta S^{(E)}$$

then

$$\Delta H^{(E)} = \Delta G^{(E)}$$

Assuming that $\Delta H^{(E)}$ has the form Ax_1x_2 , it was possible to determine A from the integral equation mentioned above and, hence, $\Delta H^{(E)}$ for 1 atm. The resulting curve is very close to the curves for $\Delta G^{(E)}$ at 80 and 90° K and it can therefore be assumed that the assumption of a regular solution is justified.

Professor W. C. Edminster (Oklahoma State University) reviewed the work carried out in recent years and planned for the immediate future in the U.S.A. to overcome the 'enthalpy ignorance', the significance of which had been fully realized in that country where, it was estimated, it was costing over \$1,500,000 annually.

Enthalpies of gaseous and liquid mixtures can be computed by way of thermodynamic relations from accurate P - V - T - X data or determined experimentally by calorimetric measurements. The results can be used to develop compilations of partial enthalpies as functions of temperature, pressure, and composition for each component. The difficulty is to find a suitable composition parameter.

The former method was used twenty years ago by Benedict and colleagues, who developed an 8-constant

empirical equation of state, correlated the resulting fugacity coefficients for light hydrocarbons, and used these for calculating enthalpies of mixtures. The same fugacity correlations were later used by Edminster and Canjar to compute partial enthalpies. An attempt was made to generalize these in terms of reduced parameters, but extrapolation to obtain partial enthalpies of other substances in different mixtures was found to be impossible.

The correlation of ΔH values computed for specific systems directly from P - V - T - X data appears more advantageous than the reverse procedure.

A project to obtain enthalpies of mixtures has been initiated in the U.S.A. by the Natural Gasoline Association. This project, which will take about 8 years to complete and will cost \$300,000, will involve experimental work at two or three universities, data correlation, theoretical work, and preparation of charts, tables, equations, and computer programmes.

Experimental work has been started at a number of places, including the Chemical Engineering Department of the University of Michigan, the Institute of Gas Technology at Chicago, and in the Chemical Engineering Laboratory at Oklahoma State University. Here Professor Edminster is intending to use an isobaric flow calorimeter, an isothermal throttling calorimeter, and an isobaric calorimeter to measure integral heats of vaporization.

Professor G. G. Haselden (Leeds University), considering ways of determining enthalpies of mixtures, stressed the importance of direct methods in view of the magnitude of the task. The measurement of Joule-Thomson coefficients provided a quick and reasonably direct method for single-phase systems. Heats of mixing and flow calorimeter methods were suitable in the two-phase region. The boiling type calorimeter tended to be inaccurate for enthalpy determinations, especially at high pressures, owing to the instability of the boiling process and the large thermal capacity of the apparatus. Work on heats of mixing had been started at Leeds University and a condensing type flow calorimeter had been built at Imperial College, London.

Summing up the contributions and the subsequent discussion, the Chairman proposed that Commission I of the International Institute of Refrigeration should take steps to stimulate work on the enthalpies of mixtures, both experimental and theoretical, the latter to include fundamental work as well as the correlation of results in a form suitable for design purposes. Co-ordination of work in progress should be encouraged both within individual countries and on an international basis. A motion embodying these proposals was carried by the meeting.

Letters to the Editors

A Proposal for a New Nuclear Demagnetization Method

KURTI, Simon, Robinson, and Spohr succeeded in 1956 in the difficult experiment of cooling nuclei of metallic copper to a temperature of 10^{-5}°K . Later on, their method was developed further and new results were published.¹ The method they used had been proposed some years previously by Gorter² and by Kurti and Simon.^{3,4} It consists of a two-stage demagnetization.

First an electronic paramagnetic salt (pill A) is cooled to about 0.01°K by ordinary adiabatic demagnetization. This heat sink is connected thermally with a pill B containing nuclei with a magnetic moment. The pill B is placed in a strong magnetic field, but the field at the electronic stage must be weak. It follows that there must be a fairly long connection between the pills. After removal of the heat of magnetization from pill B to pill A, the magnetic field is reduced and the substance of pill B cools down.

In order to overcome the difficulty of the heat transport between the pills, Kurti et al. chose copper for the material of the link and also for pill B.

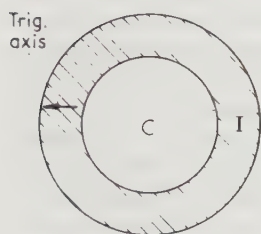


Figure 1. Principle of the arrangement with core C and shell I

It would be advantageous if protons could be taken as the nuclear stage instead of copper nuclei. Protons have a magnetic moment which is 3.8 times that of both the copper isotopes. Thus the entropy reduction would be 15 times larger at the same initial field and temperature, as this reduction is proportional to the square of the magnetic moment. However, the difficulty then is the heat transfer from the nuclear to the electronic stage.

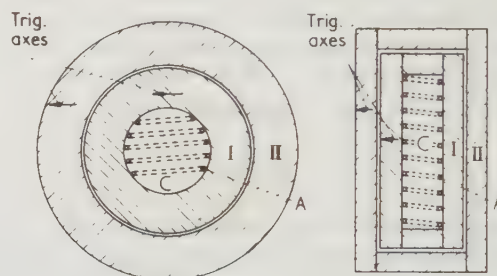
The problem might be solved by the application of monocrystals with an anisotropic g factor, such as a number of paramagnetic salts of the rare earths group possess. With these crystals a low temperature can be achieved by rotation of the magnetic field.⁵ This property suggests the idea of a pill built up of a core containing the nuclear stage (protons) surrounded by a shell made of one of the above-mentioned paramagnetic rare earth crystals (Figure 1). Now the nuclear substance is on all sides in heat contact with the electronic substance.

Cerium magnesium nitrate is a suitable substance for shell I. It has a trigonal structure, and the g factor perpendicular to the trigonal axis (g_{\perp}) is much larger than the g

factor parallel to this axis (g_{\parallel}). Very low temperatures (0.01°K) can be obtained by magnetizing this salt in a field perpendicular to the trigonal axis, and demagnetizing it by rotation of the field to a direction parallel to the trigonal axis.

The experimental procedure, in principle, is then as follows:

- (1) The pill is magnetized perpendicularly to the trigonal axis with the strongest possible field at the lowest temperature attainable by pumping liquid helium.
- (2) The heat contact between pill and bath is broken.
- (3) The magnetic field is turned slowly in the direction of the trigonal axis, resulting in a reduction of the temperature of the shell I, which cools in its turn the core C.
- (4) The magnetic field is reduced to zero and the core cools down.



C: Lanthanum magnesium nitrate I: Cerium magnesium nitrate
II: Neodymium magnesium nitrate

Figure 2. Two different examples consisting of core C, shell I, guard shell II, and coil A

We intend to use a pill with a guard ring. Two different examples are given in Figure 2, showing cross-sections parallel to the (vertical) cryostat axis. The core C is made of a monocrystal of, for example, lanthanum magnesium nitrate. The protons of the crystallization water will be magnetized. Shell I, which must have as good a heat contact as possible with core C, is made of one or more monocrystals of cerium magnesium nitrate. A fair heat contact can be achieved by grinding the outer surface of C and the inner surface of the shell I, and by applying some silicon grease or other cement between them.⁶⁻⁸

Shell II is made of one or more monocrystals of neodymium magnesium nitrate with the trigonal axis parallel to that of the cerium salt and mounted in such a way as to have bad heat contact with shell I. As $g_{\parallel} \ll g_{\perp}$ for this salt also, it too is cooled by rotation of the field. The specific heat of the neodymium salt is much higher than that of the cerium, so it can serve well as a guard shell.

In order to measure the temperature of the core C, a coil A is provided on C and thus inside shell I; it is the secondary coil of a Hartshorn bridge.

The heat transfer of the shell I to the lattice of core C can be made fairly high. That of the lattice to the protons of the core is very low in accordance with the very long lattice-nuclei relaxation time. This relaxation time, however, can be reduced by the incorporation of paramagnetic ions in the core C as indicated by Bloembergen,⁹ by Rollin and Hatton,¹⁰ and by Khutsishvili¹¹ (either Cr³⁺ in the alum, or neodymium in the nitrate).

These paramagnetic contaminations will have a large effect on the susceptibility of the core. Kurti,¹² however, showed that below about 0.02°K the susceptibility of the impurities becomes independent of temperature, so that below that temperature any change in susceptibility can be ascribed to the nuclear spin system.

It is hoped that Kurti's conclusion will also remain substantially correct in our experiments, although the amount of impurities will be much higher.

If the longitudinal relaxation time t_1 of protons or other nuclei in an anisotropic (eventually diluted) salt such as cerium or neodymium magnesium nitrate were of the order of several minutes at temperatures of about 0.01°K, a much simpler procedure for the nuclear cooling could be followed. Then, after slow rotation cooling of the salt, one should have to wait only a reasonable time for the electron system to cool the proton system. Following this, the demagnetization would cool the nuclei to a very low temperature. The warming up of the nuclear by the electronic system would be slow enough to allow the temperature measurement.

A more detailed account of this proposal will appear in the proceedings of Commission I of the International Institute of Refrigeration, held at Eindhoven on 28-30 June 1960.

B. S. BLAISSE

Laboratorium voor Technische Fysica,
Delft,
Holland.

(18 July 1960)

REFERENCES

1. KURTI, N., ROBINSON, F. N. H., SIMON, F. E., and SPOHR, D. A. *Nature, Lond.* **178**, 450 (1956); KURTI, N. *Sci. Progr.* **45**, 401 (1957); KURTI, N. *Phys. Today* **11**, 12 (1958); KURTI, N. *J. Phys. Radium* **17**, 85 (1956); HOB DEN, M. V., and KURTI, N. *Phil. Mag.* **4**, 1092 (1959)
2. GORTER, C. J. *Phys. Z.* **35**, 923 (1934)
3. KURTI, N., and SIMON, F. E. *Proc. roy. Soc.* **A151**, 610 (1935)
4. SIMON, F. E. *C. R. du Congrès sur le Magnétisme, Strassbourg*, **3**, 1 (1939)
5. WHEATLEY, J. C., and ESTLE, T. L. *Phys. Rev.* **104**, 264 (1956)
6. COOKE, A. H., MEYER, H., and WOLF, W. P. *Proc. roy. Soc.* **A233**, 536 (1956)
7. MIEDEMA, A. R., POSTMA, H., VAN DER VLUGT, N. J., and STEENLAND, M. J. *Physica* **25**, 509 (1959)
8. HART, H. R., JR., and WHEATLEY, J. C. *Proc. Delft Conf. Annexe 1958-1. Suppl. Bull. I.I.F.*, p. 311
9. BLOEMBERGEN, N. *Physica* **15**, 386, 426 (1949)
10. ROLLIN, B. V., and HATTON, J. *Phys. Rev.* **74**, 346 (1948)
11. KHUTSISHVILI, G. R. *J. exp. theor. Phys.* **31**, 424 (1956), *Soviet Phys. JETP* **4**, 382 (1957)
12. KURTI, N. *Sci. Progr.* **179**, 401 (1957)

The Cooling of Specimens for Calorimetry at Very Low Temperatures

ONE very tricky problem in calorimetry at extremely low temperatures is the cooling of a specimen which, for the measurement, is thermally insulated inside a vessel such as V in Figure 1, the vessel itself being submerged in, for example, a bath of liquid helium. This cooling may be effected either by temporarily introducing an exchange gas, such as helium, into V, or by making a thermal contact between the specimen E and the wall through a mechanical process.

The exchange gas method has been generally used for a long time and yields excellent results with metals and alloys.¹ However, it has the disadvantage of requiring pumping for a considerable time after the right temperature has been reached. The vacuum channel must have a very small diameter in order to prevent radiation heat from entering and, moreover, the exchange gas is adsorbed on the specimen. If the specimen has a large area

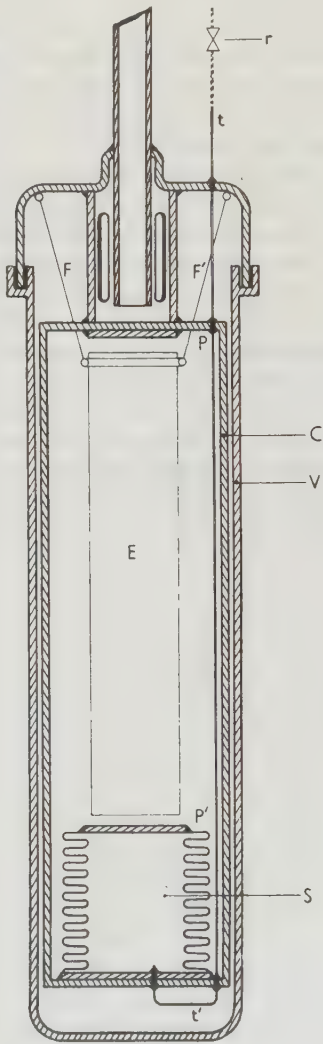


Figure 1.

(powdered or sintered products), the quantity of gas so adsorbed may be considerable and may cause disturbances which are not well understood. If measurements are made at very low temperatures, where the specific heat of the solid is itself considerably reduced, the calorific capacity of the adsorbed fluid, which varies only little as a function of the temperature, becomes an important correction.

In order to be efficient, the *mechanical* contact requires considerable pressure, as Berman² has shown in his work on the effect of contact force on conductance. Sometimes the force is transmitted directly from the outside, but preferably it is amplified at the low temperature. The most common mechanical method consists of locking the specimen in a clamp kept at the temperature of the vessel V controlled by vertical traction.³ Because of the clamp, and in spite of the amplification, the size of the control wire used remains fairly important, bringing an amount of heat which is not negligible. Also, since the clamp is necessarily rather massive, a fairly long time elapses before its temperature is reduced to that of the vessel V.

Finally, as it is required that, at the moment when the contact is broken, no vibrations which might generate heat are created in the specimen, it is necessary to break the contact very gradually, the solid frictions in the transmission are therefore undesirable.

In our method, described in the following, a *hydraulic* contact control is used: the force is exerted by means of a metal bellows S, made of tombac, which is simply inflated with helium. The filling is effected through a capillary t-t'. The force which can be applied is of the same order of magnitude as that applied with a clamp. With the tombac bellows used by us, with an inner diameter of 25 mm, and at a pressure of 4 kg/cm², the force is 20 kg. Under the effects of the pressure, the bellows expands and pushes the specimen E, suspended on the nylon threads F and F', against the plate P at the upper part of the frame C. In the case shown in the drawing, C has the

same temperature as V. The descent of the bellows is controlled by a fine regulating valve, r, and the movement of a few millimetres which will break the contact can be effected as slowly and progressively as may be desired.

Without taking any special precautions regarding contacting surface at P and P' or on the specimen, we have already been able to effect breaks entailing a liberation of heat of only 100–200 ergs using this method. That is, the heat release is of the same order of magnitude as that obtained with the most favourable contact surfaces by the mechanical methods used previously (several hundred ergs). As the capillary is located in liquid helium, all thermal disturbances are eliminated. Finally, the device is far simpler than the mechanical arrangements proposed hitherto.

This cooling method was of particular use in some work we are carrying out on sintered beryllium oxide which, being an insulator with a particularly high Debye temperature, has a very low specific heat: a 65 g specimen at 2° K has a calorific capacity of only 4×10^{-5} joules per degree.

Université de Grenoble,
France.

J. ASLANIAN
L. WEIL

(26 September 1960)

REFERENCES

1. GOODMAN, B. B., HILLAIRET, J., VEYSSIE, J. J., and WEIL, L. *C. R. Acad. Sci., Paris* **250**, 542 (1960); GOODMAN, B. B., HILLAIRET, J., VEYSSIE, J. J., and WEIL, L. *7th Int. Conf. on Low Temperature Physics* **22**, 1 (Toronto, 1960)
2. BERMAN, R. *J. appl. Phys.* **27**, 318 (1956)
3. BURNS, J. H., OSBORN, D. W., and WESTRUM, E. F. *J. chem. Phys.* **33**, 387 (1960); WESTRUM, E. F., HATCHER, J. B., and OSBORNE, D. N. *J. chem. Phys.* **21**, 419 (1953); WEBB, F. J., and WILKS, J. *Proc. roy. Soc.* **A230**, 549 (1955)

Book Reviews

Cryophysics. K. Mendelssohn. *'Tracts on Physics and Astronomy' Series.* (Interscience Publishers, 1960) 192 pages. Cloth \$4.50 (34s.); Paper \$2.50 (19s).

Within the past five years the literature of low temperature physics has grown at a remarkable rate. In addition to review articles on particular topics in the new *Handbuch der Physik* and in *Advances in Solid State Physics*, we now have two 'Progress' series devoted specifically to the field, each of which has so far produced two volumes, and several books dealing with liquefiers and low temperature techniques. To supplement these, voluminous conference reports appear at regular intervals. But for the undergraduate or the beginner in research who seeks a broad general survey of the subject, none of these is suitable, at any rate for first reading. The latest edition of Jackson's excellent monograph appeared in 1955; much has happened since then, and there has been a real need for a more up-to-date introductory text. Dr. Mendelssohn's new book has been written in an attempt to fill this need. Within the space of 180 pages, he has managed to touch on practically every topic in the field, including many of very recent development. The chapter headings follow roughly the traditional pattern—cryogenics, thermometry, specific heats, magnetism, transport phenomena, superconductivity, and helium—and sections are included on nuclear orientation, dielectric heat conduction, cryotrons, superconductivity theory (with a rather lukewarm reference to the Bardeen-Cooper-Schrieffer theory), turbulence in liquid helium, and liquid helium-3; an additional chapter entitled 'Miscellaneous' covers the melting curve, thermal expansion, mechanical properties, trapped free radicals, bubble chambers, and masers. Each chapter ends with a useful list of references to recent review articles.

It has not been possible to cover this wide range of topics without some sacrifice, of course. As the author states in his preface 'detailed treatment has been avoided throughout', but to achieve even a superficial survey in the space available he has had to write with the greatest economy. At many points a few extra words would have added greatly to the clarity, and in some places the beginner is likely to be seriously puzzled. For example, on page 21, in discussing the Oxford work on nuclear demagnetization it is remarked in passing that 'the rate at which the measured nuclear susceptibility decreased again was high', but the implications of this remark remain obscure until page 26. Again, on page 62, the sudden appearance of the word 'ferrimagnetism', once and without explanation, is likely to confuse rather than enlighten the student, unless he supposes it to be a misprint. On page 44, in the section on electronic specific heat, it is not made clear that equation (3-4) for an ideal Fermi-Dirac gas applies only when the departure from classical behaviour is very small, and is quite irrelevant to the subsequent discussion of electrons in a metal. And on page 168, the student is liable to be

puzzled by the dimensionless 'energy gaps' Δ and δ . These obscurities, and others, are possibly inevitable when so much is compressed into the space available, but they make it difficult to recommend the book unreservedly to the beginner. For those who already have reasonable familiarity with the subject, however, it can be recommended as a useful summary of recent developments.

R. G. CHAMBERS

Liquid Helium. K. R. Atkins. *'Monographs on Physics' Series.* (Cambridge University Press) 312 pages. 60s.

Most of the distinctive characteristics of liquid helium-4 were essentially known fifteen years ago or more, and much of the basic theory for understanding them laid down. Strong elements of mystery and uncertainty were subsequently attacked with vigour, but it was only a few years ago that a theoretical picture emerged, supported by experiment, which promised to lead to a completely satisfactory solution. Professor Atkins' book is thus well timed, coming as it does shortly after this great advance in the subject. While there are undoubtedly many interesting discoveries still to be made (and some have been made since the book was written), the approach seems now to be rather one of a mopping-up operation than a fundamental attack. As the author believes, the ultimate solution will probably be along similar lines to those he describes, and it will thus be some time before his book becomes seriously out of date.

The book inclines to explain the current situation rather than give an historical exposition, an approach which has its advantages in a subject with a long and sometimes confusing history. It makes easy and stimulating reading, and succeeds in giving a wide survey of work on helium-II, although naturally one may not always agree with the emphasis placed on the various aspects. The treatment of thermodynamics and vortex line theory forms a particularly useful introduction to the subject, although the impression may sometimes be received that the observations are better understood than is in fact the case. Two chapters on liquid helium-3 and on liquid helium-3-helium-4 mixtures are also included. Fundamental discoveries about helium-3 are being made at a rapid pace and this section has already become somewhat out of date. It still provides a most useful and interesting introduction because of the author's clear exposition. The book as a whole will certainly become compulsory reading for research students—it is the only book on the subject of which this can be said—and a stimulating, if not quite exhaustive, reference for others.

D. F. BREWER

Bibliography

The following list of papers and letters concerning low temperature physics and engineering has been compiled from a wide range of periodicals and covers the period May-August 1960. A list of recent publications will be a regular feature of CRYOGENICS.

- ABRAGAM, A. 'Sur la Possibilité d'observer des Phénomènes Coopératifs en Magnétisme Nucléaire.' *C. R. Acad. Sci., Paris* **251**, 225 (1960)
- ADAIR, T. W., SQUIRE, C. F., and UTLEY, H. B. 'High Field Solenoid Magnet with Liquid Nitrogen Cooling.' *Rev. sci. Instrum.* **31**, 416 (1960)
- ALSTON, M. H., CUNDY, D. C., EVANS, W. H., NEWPORT, R. W., and WILLIAMS, P. R. 'A 10 in. Diameter Liquid Hydrogen Bubble Chamber.' *Phil. Mag.* **5**, 146 (1960)
- AMBLER, E., and PLUMB, H. 'Use of Carbon Resistors as Low Temperature Thermometers in the Presence of Stray r.f. Fields.' *Rev. sci. Instrum.* **31**, 656 (1960)
- ANON. 'Low-Temperature Strengths of Metal Adhesives.' *Nat. Bur. Stand. Tech. News Bull.* **44**, 41 (1960)
- ANON. 'Results of Free Radicals Research.' *Nat. Bur. Stand. Tech. News Bull.* **44**, 100 (1960)
- ANON. 'Low Temperature Experiments.' *World Refrig. & Air Condit.* **11**, No. 7, 48 (1960)
- ARKHIPOV, R. G., and SHAL'NIKOV, A. I. 'On the Problem of the Motion of Charges in Liquid Helium II.' *J. exp. theor. Phys.* **37**, 1247 (1959), *Soviet Phys. JETP* **37**, 888 (1960)
- ATTARD, A. E., and AZAROFF, L. V. 'Liquid-nitrogen Cryostat for Single-crystal X-ray Diffraction.' *J. sci. Instrum.* **37**, 238 (1960)
- AUTLER, S. H. 'Superconducting Electromagnets.' *Rev. sci. Instrum.* **31**, 369 (1960)
- BECHGRER, R., and REIMANN, R. 'La Résonance des Protons du Charbon Actif à Basse Température.' *C. R. Acad. Sci., Paris* **250**, 3159 (1960)
- BELLAMY, E. H., HOGG, W. R., and MILLER, D. 'A Thin Liquid Hydrogen or Deuterium Target.' *Nuclear Instrum.* **7**, 293 (1960)
- BENEDEK, G. B., and KUSHIDA, T. 'Nuclear Magnetic Resonance in Antiferromagnetic MnF_2 under Hydrostatic Pressure.' *Phys. Rev.* **118**, 46 (1960)
- BLANK, C., and EDWARDS, M. H. 'Dielectric Breakdown of Liquid Helium.' *Phys. Rev.* **119**, 50 (1960)
- BROWN, N. L., and BARFIELD, R. N. 'Shield Coaxial Leads for Low Temperature Electrical Measurements.' *Rev. sci. Instrum.* **31**, 517 (1960)
- BRUECKNER, K. A., SODA, T., ANDERSON, P. W., and MOREL, P. 'Level Structure of Nuclear Matter and Liquid He^3 .' *Phys. Rev.* **118**, 1442 (1960)
- BRYANT, C. A., and KEESOM, P. H. 'Specific Heat of Indium below $1^\circ K$.' *Phys. Rev. Lett.* **4**, 460 (1960)
- BUCKMASTER, M. A., and LEGGE, J. 'Double Glass Dewar with a Three-Wall Tail.' *Rev. sci. Instrum.* **31**, 776 (1960)
- BUDWORTH, D. W., HOARE, F. E., and PRESTON, J. 'The Thermal and Magnetic Properties of Some Transition Element Alloys.' *Proc. roy. Soc.* **A257**, 250 (1960)
- BULATOVA, R. F., KOGAN, V. S., and LAZAREV, V. G. 'Mutual Solubility of Hydrogen and Deuterium at $4.2^\circ K$.' *J. exp. theor. Phys.* **37**, 1492 (1959), *Soviet Phys. JETP* **37**, 1058 (1960)
- CAPE, J., and JACOBS, G. 'Low-Temperature Properties of H , V , and F Centers in KCl and KBr .' *Phys. Rev.* **118**, 946 (1960)
- CARERI, G., MODENA, I., and SANTINI, M. 'New Measurements of the Spin-Lattice Relaxation Time in Liquid Helium 3.' *Nuovo Cim.* **XVI**, 782 (1960)
- CHELTON, D. B., DEAN, J. W., and BIRMINGHAM, B. W. 'Closed Circuit Liquid Hydrogen Refrigeration System.' *Rev. sci. Instrum.* **31**, 712 (1960)
- COHEN, M. 'Relation between Inelastic Neutron Scattering and Thermodynamic Functions of Liquid Helium.' *Phys. Rev.* **118**, 27 (1960)
- COLES, B. R., and GRIFFITHS, D. 'Ferromagnetic and Antiferromagnetic Behaviour in the Second Transition Group.' *Nature, Lond.* **187**, 226 (1960)
- CORRUCCINI, R. J. 'Interpolation of Platinum Resistance Thermometers, 20° to $273.15^\circ K$.' *Rev. sci. Instrum.* **31**, 637 (1960)
- COURPRON, C., LOCHET, R., MEYER, Y., and ROUSSET, A. 'Luminescence Moléculaire du Benzène en Solution Étendue dans le Cyclohexane à la Température de L'Azote Liquide.' *C. R. Acad. Sci., Paris* **250**, 3095 (1960)
- CRANGLE, J. 'Ferromagnetism in Pd-rich Palladium-Iron Alloys.' *Phil. Mag.* **5**, 335 (1960)
- CRITTENDEN, E. C., JR., COOPER, J. N., and SCHMIDLIN, F. W. 'The "Persistor"—A Superconducting Memory Element.' *Proc. Inst. Radio Engrs, N.Y.* **48**, 1233 (1960)
- CUNDY, D. C., EVANS, W. H., HADLEY, D. W., MASON, P., NEWPORT, R. W., SMITH, J. R., and WILLIAMS, P. R. 'Systematic Track Distortion in a 10 in. Diameter Liquid Hydrogen Bubble Chamber.' *Phil. Mag.* **5**, 154 (1960)
- DANIELS, J. M., and RIECKHOFF, K. E. 'Spin Lattice Relaxation in Neodymium Ethylsulphate at Liquid Helium Temperatures.' *Canad. J. Phys.* **38**, 604 (1960)
- DEBEAUVAIS-WACK, M. 'Etude Comparée de la Sensibilité des Émulsions Ionographiques Entre $+20$ et $-196^\circ C$ Vis-à-vis du Rayonnement Lumineux et du Rayonnement α du Polonium.' *C. R. Acad. Sci., Paris* **251**, 79 (1960)

- DRESSELHAUS, G., and DRESSELHAUS, M. S. 'Surface Impedance of a Superconductor in a Magnetic Field.' *Phys. Rev.* **118**, 77 (1960)
- DRESSLER, K., and SCHNEPP, O. 'Absorption Spectra of Solid Methane, Ammonia, and Ice in the Vacuum Ultraviolet.' *J. chem. Phys.* **33**, 270 (1960)
- EMERY, V. J., and SESSLER, A. M. 'Possible Phase Transition in Liquid He³.' *Phys. Rev.* **119**, 43 (1960)
- FAIRBANK, H. A., and LEE, D. M. 'Thermal Conductivity of 70-30 Cupro-nickel Alloy from 0.3° to 4.0° K.' *Rev. sci. Instrum.* **31**, 660 (1960)
- FLOTOW, H. E., and LÖHR, H. R. 'The Heat Capacity and Thermodynamic Functions of Uranium from 5 to 350° K.' *J. phys. Chem.* **64**, 904 (1960)
- FLYNN, T. M. 'Pilot Plant Data for Hydrogen Isotope Distillation.' *Chem. Engng Progr.* **56**, No. 3, 37 (1960)
- FRADKOV, A. B. 'A Helium Cryostat without Cooling by Liquid Nitrogen.' *C. R. Acad. Sci., U.R.S.S.* **133**, 817 (1960)
- FRANCHETTI, S. 'Some Remarks on the Theory of the Liquid Helium Film.' *Nuovo Cim.* **XVI**, 1158 (1960)
- GAUMER, R. E., and HEER, C. V. 'Atomic Heat of Sodium Metal from 0.4 to 2° K.' *Phys. Rev.* **118**, 955 (1960)
- GOLDSTEIN, L. 'Thermal Properties of Solid He⁴.' *Phys. Rev. Lett.* **5**, 104 (1960)
- GOODKIND, J. M., and FAIRBANK, W. M. 'Nuclear Spin Relaxation in Solid He³.' *Phys. Rev. Lett.* **4**, 458 (1960)
- GRAMBERG, G. 'Absorptionsspektrum und Zeeman-Effekt von kristallinen Dysprosiumsätzen bei tiefen Temperaturen.' *Z. Phys.* **159**, 125 (1960)
- GROHMANN, I., HELLWEGE, K., and KAHLE, H. G. 'Kernhyperfeinstruktur im Absorptionsspektrum eines kristallinen Salzes.' *Naturwiss.* **47**, 277 (1960)
- HÄNNY, J. 'Industrial Plant for the Production of Heavy Water.' *Kaltetechnik* **6**, 158 (1960)
- HEASTIE, R., and LEFEBVRE, C. 'Phase Equilibria in Condensed Mixtures of Argon and Xenon.' *Proc. phys. Soc. Lond.* **76**, 180 (1960)
- HEMPSTEAD, C. F., and BOWERS, K. D. 'Paramagnetic Resonance of Impurities in CaWO₄. I. Two S-State Ions.' *Phys. Rev.* **118**, 131 (1960)
- HENSHAW, D. G. 'Effect of the λ Transition on the Atomic Distribution in Liquid Helium by Neutron Diffraction.' *Phys. Rev.* **119**, 9 (1960)
- HENSHAW, D. G. 'Pressure Effect in the Atomic Distribution in Liquid Helium by Neutron Diffraction.' *Phys. Rev.* **119**, 14 (1960)
- HENSHAW, D. G. 'Structure of Liquid Oxygen by Neutron Diffraction.' *Phys. Rev.* **119**, 22 (1960)
- HONIG, A., and LEVITT, R. 'Shallow Impurity Traps and Electron Transfer Dynamics in n-Type Silicon at Liquid Helium Temperatures.' *Phys. Rev. Lett.* **5**, 93 (1960)
- HOSFORD, W. F., JR., FLEISCHER, R. L., and BACKOFEN, W. A. 'Tensile Deformation of Aluminium Single Crystals at Low Temperatures.' *Acta Metall.* **8**, 187 (1960)
- JAGGI, R., and SOMMERHALDER, R. 'Messung der Eindringtiefe an supraleitenden Hohlkörpern.' *Helv. phys. acta* **XXXIII**, 1 (1960)
- JONES, G. H. S., and HOLLIS HALLETT, A. C. 'The Specific Heat of Crystalline Quartz between 2° K and 4° K.' *Canad. J. Phys.* **38**, 696 (1960)
- JONES, G. O., and SMITH, B. L. 'The Refractive Indices of Liquid and Solid Argon.' *Phil. Mag.* **5**, 355 (1960)
- KAITMAZOV, S. D., and PROKHOROV, A. M. 'Cavities for Observing Electronic Paramagnetic Resonance at Low Temperatures.' *Prib. i Tekh. Eksper.* No. 5, 107 (1959). *Instrum. Exper. Tech.* No. 5, 808 (1960)
- KELLER, W. E., and HAMMEL, E. F., JR. 'Heat Conduction and Fountain Pressure in Liquid He II.' *Ann. Phys.* **10**, 202 (1960)
- KENNEY, V. P. 'Velocity Dependence of the Bubble Density for Charged Particle Tracks in Liquid Hydrogen.' *Phys. Rev.* **119**, 432 (1960)
- KOGAN, A. V., KUL'KOV, V. D., NIKITIN, L. P., and REINOV, N. M. 'Superconductor Magnets for Orientation of Nuclei.' *J. tech. Phys., Moscow* **29**, 1419 (1959). *Soviet Phys. Tech. Phys.* **4**, 1308 (1960)
- LAUTZ, G., and PILKUHN, M. 'Rauchmessungen an Germanium-Einkristallen im Bereich der Stossionisationseffekte zwischen 5° und 10° K.' *Naturwiss.* **47**, 198 (1960)
- LAZAREV, B. G., SUDOVTSSEV, A. I., and SEMENENKO, E. E. 'Superconductivity of Beryllium and its Low-temperature Polymorphism.' *J. exp. theor. Phys.* **37**, 1461 (1959). *Soviet Phys. JETP* **37**, 1035 (1960)
- LEVY, R. A., and ZUCKER, M. J. 'New Type of Liquid Helium Dewar System.' *Rev. sci. Instrum.* **31**, 656 (1960)
- LIEN, W. H., and PHILLIPS, N. E. 'Heat Capacity of Sodium and Potassium at Temperatures below 1° K.' *Phys. Rev.* **118**, 958 (1960)
- MACDONALD, D. K. C., PEARSON, W. B., and TEMPLETON, I. M. 'Thermo-electricity at Low Temperatures. VIII. Thermoelectricity of the Alkali Metals below 2° K.' *Proc. roy. Soc.* **A256**, 334 (1960)
- MEYER, L., and REIF, F. 'Scattering of Thermal Energy Ions in Superfluid Liquid He by Phonons and He³ Atoms.' *Phys. Rev. Lett.* **5**, 1 (1960)
- MÖSSBAUER, R. L., and WIEDEMANN, W. H. 'Kernresonanzabsorption nicht Doppler-verbreiteter Gammastrahlung in Re¹⁸⁷.' *Z. Phys.* **159**, 33 (1960)
- NOBLE, G. A. 'Saturation and Recovery of a Portion of the Electron Spin Resonance of F Centers in KCl at 4° K.' *Phys. Rev.* **118**, 1028 (1960)
- NOVIKOVA, S. I. 'Thermal Expansion of Germanium at Low Temperatures.' *Fiz. Tverd. Tela.* **2**, 43 (1960). *Soviet Phys. Solid State* **2**, 37 (1960)
- OUVER, D. J., RAYNER, M. J., and RHODERICK, E. H. 'Speed of the Superconducting-Normal Transition in Tin Films.' *Nature, Lond.* **187**, 492 (1960)
- PEARSON, W. B. 'Interpretation of Relative Thermoelectric Phenomena at Low Temperatures with Special Consideration of the Effects of Cold-Work on Copper.' *Phys. Rev.* **119**, 549 (1960)
- PEARSON, W. B. 'The Thermoelectric Power of Annealed and Cold-Worked Silver and Gold at Low Temperatures.' *Canad. J. Phys.* **38**, 1048 (1960)

- REEBER, M. D. 'Superconductivity of Dilute Indium-Mercury Alloys.' *Phys. Rev.* **117**, 1476 (1960)
- ROSI, F. D., MEYERHOFER, D., and JENSEN, R. V. 'Properties of *p*-Type GaAs Prepared by Copper Diffusion.' *J. appl. Phys.* **31**, 1105 (1960)
- RÜHL, W. 'Einfluss adsorbierter Gase auf Supraleitung und elektrische Leitfähigkeit dünner Thalliumsichten.' *Z. Phys.* **159**, 428 (1960)
- RYTER, C. 'Direct Measurement of the Electron Density at the Nucleus in Metallic Lithium at Liquid Helium Temperature.' *Phys. Rev. Lett.* **5**, 10 (1960)
- SCHNEPP, O., and DRESSLER, K. 'Absorption Spectra of Solid Xenon, Krypton, and Argon in the Vacuum Ultraviolet.' *J. chem. Phys.* **33**, 49 (1960)
- SCHNEPP, O., and DRESSLER, K. 'Photolysis of Ammonia in a Solid Matrix at Low Temperatures.' *J. chem. Phys.* **32**, 1682 (1960)
- SCHRADER, B., NERDEL, F., and KRESZE, G. 'Apparatur zur Aufnahme von Raman-Spektren fester Substanzen bei tiefen Temperaturen.' *Naturwiss.* **47**, 198 (1960)
- SHERMAN, R. H., and EDESKUTY, F. J. 'Pressure-Volume Temperature Relations of Liquid He³ from 1.00 to 3.30° K.' *Ann. Phys.* **9**, 522 (1960)
- SHOENBERG, D. 'The de Haas-van Alphen Effect in Copper, Silver and Gold.' *Phil. Mag.* **5**, 105 (1960)
- SLEESWYK, A. W. 'Device for Cyclic Plastic Deformation at Low Temperature.' *Rev. sci. Instrum.* **31**, 793 (1960)
- SWARUP, P., and MISRA, B. N. 'A Note on the Paramagnetic Resonance of Free Radicals.' *Z. Phys.* **159**, 384 (1960)
- SYDORIAK, S. G., MILLS, R. L., and GRILLY, E. R. 'PVT Anomalies in He³ near its Melting Curve.' *Phys. Rev. Lett.* **4**, 495 (1960)
- SYDORIAK, S. G., and ROBERTS, T. R. 'Vapor Pressures of He³-He⁴ Mixtures.' *Phys. Rev.* **118**, 901 (1960)
- VAN ITTERBEEK, A., PEELAERS, W., and STEFFENS, F. 'Susceptibility Measurements of Nb between Room Temperature and Liquid Helium Temperatures.' *Appl. sci. Res. Hague* **B8**, 177 (1960)
- VISWAMITRA, M. A., and RAMASESHAN, S. 'Simple Device for Growing Crystals at Low Temperatures in X-ray Cameras.' *Rev. sci. Instrum.* **31**, 456 (1960)
- WALKER, E. J., and FAIRBANK, H. A. 'Thermal Conductivity of Isotopic Mixtures of Solid Helium.' *Phys. Rev.* **118**, 913 (1960)